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ANALYTICAL
ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2473. Determination of molecular characteristics by surface techniques. J. Guastalla. *Chim. Anal.*, 1957, **39** (2), 41–52.—A detailed examination is presented of surface layers, both spread and adsorbed, in relation to their molecular structure, and their importance in analytical and industrial techniques.   W. J. WRIGHT

2474. The use of disubstituted dithiocarbamate compounds for analytical separations. G. Eckert (Siemens-Halske A.-G., München). *Z. anal. Chem.*, 1957, **155** (1), 23–35.—The di-N-substituted dithiocarbamic acids are not specific reagents, but form with many heavy metals stable complexes very sparingly soluble in water. In spite of lack of specificity, many separations are possible, (*i*) by pptn. or solvent extraction of the required metal, while interfering metals are masked by other complexing agents; (*ii*) pptn. of interfering metals, the required metal being masked if necessary; (*iii*) by means of the differing stabilities and distribution ratios of the complexes. Separations based on these principles are presented and discussed. (27 references.)   G. BURGER

2475. Diethylenetriaminepenta-acetic acid; a new complex-forming reagent. E. Wänninen (Åbo Akad., Turku, Finland). *Suomen Kem., B,* 1955, **28** (9), 146–152 (in English). Metal-chelate stability-constants have been calculated for Ca, Sr and Ba.   N. E.

2476. Variamine blue as a colorimetric reagent. L. Erdey and F. Szabadváry (Inst. für Allgemeine Chemie, Tech. Univ., Budapest). *Z. anal. Chem.*, 1957, **155** (2), 90–96.—Variamine blue can be used for the colorimetric determination of many ions whose standard potential lies above that of the reagent, *e.g.*, Fe^{3+}, Cr^{6+}, Mn^{7+}, V^{5+}, Ag^+, IO_3^- and I^-. Oxidation equivalents of different ions give the same extinction reading so that one calibration curve suffices. An aq. soln. of the reagent (0·5%) (2 to 6 ml) is added to the test soln. (0·5 to 20 μg-equiv.) in water or alcohol. The extinction is measured after 5 min. with a Pulfrich S57 filter (570 mμ). The mechanism of formation of the blue compound, the effect of changes of conditions, and interferences are discussed. A procedure is described for the estimation of Fe^{3+}, Mn^{7+}, Cr^{6+} and V^{5+} in the presence of each other.   G. BURGER

2477. Some new metallochromic indicators of the complexone type. J. Körbl and R. Přibil (Pharm. and Biochem. Res. Inst., Czech. Acad. Science, Prague). *Chem. & Ind.,* 1957, (8), 233–234.—A series of twelve 3:3′-bis-NN-di(carboxymethyl)-aminomethyl derivatives of acid - base indicators of the phthalein and sulphonephthalein groups have been prepared by condensation of 1 mole of the phthalein or sulphonephthalein dye with 2 moles of iminodiacetic acid and 2 moles of formaldehyde. Their colour changes, and characteristics as complexometric indicators, are described.
                              W. J. WRIGHT

2478. Adsorption properties of the adsorbent Anionite M and its use in qualitative analysis. V. M. Peshkova and V. Ya. Býkova. *Sb. Stud. Rabot Mosk. Tekhnol. Inst. Myas. i. Moloch. Prom.,* 1956, (4), 59–62; *Ref. Zhur., Khim.,* 1956, Abstr. No. 71,915.—The adsorbent was saturated for 24 hr. with 5% alkali and washed with water till neutral. The ions Cl^-, SO_4^{2-}, Br^- and $S_4O_3^{2-}$ pass through completely, and S^{2-} are adsorbed. Anionite M may be used for the removal of S^{2-} from soln. of the cations of the first and second groups, after treatment with sulphide in the classical qual. analysis.   C. D. KOPKIN

2479. Separation of ions in a drop with the Weisz ring-oven. L. Serrano Berges (Zaragoza Univ., Spain). *Inf. Quim. Anal.*, 1957, **11** (1), 13–18.—The use of this oven (*cf.* Weisz, *Anal. Abstr.*, 1954, **1**, 2603) to separate sol. from insol. components in a spot on a filter-paper, without undue dilution of the former, is illustrated with reference to the separation of Cu, Pb or Sb (after fixing as sulphides) from Fe or Ni.   L. A. O'NEILL

2480. Acid - base equilibria in glacial acetic acid. IV. Quantitative interpretation of acid - base titrations in glacial acetic acid. I. M. Kolthoff and S. Bruchenstein (Univ. of Minnesota, Minneapolis, U.S.A.). *J. Amer. Chem. Soc.*, 1957, **79**, 1–7.—Equations governing the shape of potentiometric titration curves of bases in anhyd. acetic acid have been derived and verified experimentally. The paradoxes in the classical work of Conant, Hall, and Werner have been explained, and it is possible to predict the shape of the titration curve of urea with $HClO_4$, the e.m.f. of the pure salt soln., and the e.m.f. change in the vicinity of the equivalence point in the titration of Na acetate with $HClO_4$. It has also been possible to establish the relationship determining the ratio of acid to base colour of an indicator in acetic acid titrations. The colour of 1-naphtholbenzein in diethylaniline perchlorate and sodium perchlorate was accurately predicted.
                              C. A. SLATER

2481. A colorimetric titration method for the precise estimation of materials absorbing in the u.v. region. R. Fauss (Org.-anal. Lab. der Farbenfabr., Bayer A.-G., Leverkusen). *Z. anal. Chem.*, 1957, **155** (1), 11–20.—An expression is derived for the error in a colorimetric estimation with a photoelectric absorptiometer. The error is smallest when the absorption reading for the sample is compared with that of a standard soln. of the same concn. instead of that of the solvent. A metal cell is described which is fitted with quartz windows and a stirrer. A measured quantity of standard soln. of

concn. lower than that of the sample, sufficient to cover the windows, is placed in the cell, which fits into a spectrophotometer. The instrument is adjusted to give a null reading at max. absorption, a measured quantity of sample is added by pipette through the lid, and the mixture is titrated with pure solvent until the null reading is restored. The method does not depend on the validity of Beer's law.   G. BURGER

2482. Recent advances in "dead-stop end-point" titrimetry. J. T. Stock (Chem. Dept., Univ. of Connecticut, Storrs, U.S.A.). *Metallurgia, Manchr,* 1957, **55**, 48–52.—A review is presented of the recent literature dealing with apparatus, basic principles, determination of water (with Karl Fischer reagent), titrations involving metal ions, and various miscellaneous applications. (65 references.)   S.C.I. ABSTR.

2483. Coulometric titrations with ethylene-diaminetetra-acetic acid. H. H. Stein. *Dissert. Abstr.,* 1956, **16** (12), 2326.—Titrations are performed by adding Fe^{III} samples to a generator electrolyte $0.02 M$ in Fe^{III} - EDTA and M in $SO_4{}^{2-}$ at pH 3 and electrolysing the soln. between a platinum cathode and an isolated zinc anode. At the end-point of the titration Fe^{II} is formed in an amount equiv. to the Fe^{III} added. End-points are determined potentiometrically by means of a platinum indicator electrode. The precision and accuracy of the method are $\simeq 0.2\%$. For the titration of iodine, Fe^{II} - EDTA produced at a platinum electrode by the reduction of a generator electrolyte $0.02 M$ in Fe^{III} - EDTA and $0.02 M$ in Zn^{II} - EDTA in an acetate medium at pH 6 was found to be satisfactory. Methods are also given for the titration of Cd, Ca, Mn, Zn, Co and Ni.   N. E.

2484. Ferrous and ceric ions as dual intermediates in coulometric titrimetry. Effect of current density on titration efficiency of electrically generated ceric ions. A. J. Fenton, jun., and N. H. Furman (Frick Chem. Lab., Princeton Univ., N.J., U.S.A.). *Anal. Chem.,* 1957, **29** (2), 221–223.—Between the limits of 1 and 13 mA per sq. cm, the efficiency of generating Ce^{4+} from Ce^{3+} is $\ll 99.7\%$, assuming the generation of Fe^{2+} from Fe^{3+} to be 100% efficient. Outside these limits the efficiency decreases. Without the addition of H_3PO_4 to the system, much greater errors occur.   J. H. WATON

2485. The accurate chronometric micro-determination of the concentration of solutions. E. K. Nikitin and E. N. Ponomareva. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR,* 1956, **7** (10), 223–233; *Ref. Zhur., Khim.,* 1956, Abstr. No. 71,890.—The chronometric titration method, as applied to the chain reaction between $SO_3{}^{2-}$ and $IO_3{}^-$, depends on the determination of the commencement and conventional end-point of the reaction, *i.e.*, on the accurate measurement of the period of induction, the end of which will be noted by a coloration, cloudiness or a discoloration. After appropriate treatment, the soln. to be analysed is titrated in a vol. of 1 ml with the reagent added dropwise from a microburette. The concn. being sought is determined by the times of induction of the soln. and of control soln. Formulae are given for the calculation of the concn. of soln. of $K_2S_2O_5$ and KIO_3. The error is $> \pm 1.0\%$. The method may be used for the determination both of the primary soln. and of an added soln. which affects the rate of the given reaction.   C. D. KOPKIN

2486. Gas - liquid chromatography in a plastics analytical laboratory. J. Haslam and A. R. Jeffs (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *J. Appl. Chem.,* 1957, **7** (1), 24–32. —Applications to the examination of monomers, depolymerisation products and adhesives are given. The use of dinonyl sebacate as the stationary liquid phase for the determination of small amounts of methyl*cyclo*hexane in light petroleum is described.   K. A. PROCTOR

2487. Evaluation of molecular weight by identification of the constituents in gaseous-phase chromatography. A. Liberti, L. Conti and V. Crescenzi (Inst. of Gen. and Inorg. Chem., Univ. of Rome). *R.C. Accad. Naz. Lincei,* 1956, **20**, 623–629.— The difference in density caused by the presence in the eluting gas of a component eluted from a gas-chromatography column is measured by means of a differential manometer system of the type developed by Martin and James (*Biochem. J.,* 1956, **63**, 138). By employing a mixture of an unknown gas with a known gas as an internal standard, and by eluting with two different gases, the mol. wt. of the unknown gas can be computed with a mean reproducibility of $< 2\%$.   J. H. WATON

2488. Spectrographic analysis with standard calibration curves. I. S. Fishman. *Uch. Zap. Kazansk. Univ.,* 1955, **115** (12), 41–56; *Ref. Zhur. Khim.,* 1956, Abstr. No. 65,218.—In the absence of a set of standards, the quant. analysis of alloys is possible from one standard at a known angular coeff. ($\tan \alpha$) of the standard calibration curve. $\tan \alpha$ is taken from a calibration curve, obtained from several standards and making allowance for the background, produced by the same method in any laboratory. The value of $\tan \alpha$ is accurately reproducible in the analysis of a not very wide range of concn. and with the correct standard composition, which is controlled by the agreement in $\tan \alpha$ for const. standards and their soln. The exposure must be in the limits of the horizontal portion of the sparking curve. It is assumed that the self-absorption of the line depends only on its intensity. The value of $\tan \alpha$ does not depend on the characteristics of the generator. In analyses by one standard, the intensities of the analytical lines must be close to the intensities used in constructing the calibration curve. For this purpose there has been established an a.c. "standard arc" between copper electrodes under rigidly defined conditions. The equality, established when obtaining the calibration curve, of the intensities of any copper line and an analytical line at a definite concn. enables the influence of self-absorption on $\tan \alpha$ to be allowed for in any laboratory.   C. D. KOPKIN

2489. Calculation of the errors of spectrographic analysis by current measurements. II. I. S. Fishman and A. L. Stolov. *Uch. Zap. Kazansk. Univ.,* 1955, **115** (12), 57–71; *Ref. Zhur., Khim.,* 1956, Abstr. No. 65,219.—A mathematical analysis is made of the errors of determination by the three-standards method. Apart from its direct use for the calculation of errors, the given formula leads to certain deductions, which have some significance for the technique of spectrographic analysis. The min. error of the analysis is found when the standards are disposed at the edges of the concn. interval, symmetrically to the centre. The error of determinations increases from the centre to the edges of the concn. interval. In double photography

of the spectra, increase of the number of standards to more than 6 or 7 does not lower the error of the analysis very much. It is more rational to photograph a smaller number of standards but to increase the number of exposures of each. An increase in the number of exposures of the sample is more effective than increasing those of standards. On the basis of a mathematical analysis of the errors of the three-standards method and the control-standard method, the conclusion is drawn that the latter method has the greater accuracy. (See also *Ref. Zhur., Fiz.*, 1955, 15,618.)   C. D. KOPKIN

2490. Absorption spectrometry of acids and bases in alcoholic solution. V. C. Farmer and R. H. Thomson (Macaulay Inst. for Soil Res., Craigibuckler, Aberdeen). *Chem. & Ind.*, 1957, (4), 112–113.—The spectra of acid substances measured in alcohol solution may be modified by the ionisation of the acids by traces of basic impurities initially present in the solvent. Most samples of methanol and ethanol are probably contaminated in this way. A sample of ethanol commercially purified for absorption spectrometry, and used to determine the u.v. spectra of some 4-hydroxycoumarins, was found to be contaminated by a concn. of base equiv. to $3 \times 10^{-4} N$. Ions of Na, K and Ca accounted for a concn. of $6 \times 10^{-5} N$, and were probably introduced at a purification stage involving heating under reflux with KOH. It is recommended that instead of attempting to measure absorption spectra of acids or bases in strictly neutral soln. of hydrophilic solvents, enough strong acid (to $\Rightarrow 0 \cdot 1 N$) or alkali should be added to ensure that only the ionised or non-ionised form is present as desired. Correction must be made for the absorption of the added acid or alkali.   G. S. ROBERTS

2491. Variation of the optimal range of extinction in photo-electric absorptiometry by non-photometric factors. J. Agterdenbos (Lab. für Anal. Chem., Univ. Amsterdam, Holland). *Z. anal. Chem.*, 1957, **154** (6), 401–406.—Three of the sources of variance in absorptiometric determinations by the substitution method are considered. (*a*) Errors in measuring the transmission give a standard deviation s_t. (*b*) Errors which are directly proportional to concn. give a standard deviation s_p; this occurs when the stoicheiometry of colour formation varies. (*c*) Errors independent of concn. give a standard deviation s_i; this occurs when the sample or the reagents used give interfering colours. The observed variance of the concn. measurements is given by—

$$s^2 = \left(\frac{0 \cdot 4343\, s_t}{E\ 10^{-E}}\right)^2 + (s_p)^2 + \left(\frac{s_i}{E}\right)^2$$

If only (*a*) is considered, a graph relating s ($\propto \mathrm{d}c/c$) and E shows a shallow minimum for values of E in the range $0 \cdot 2$ to $0 \cdot 8$. Graphs and tables are presented to show that the relative error increases and that the optimal extinction for min. relative error shifts from $0 \cdot 4343$ to higher values when (*b*) and (*c*) are also taken into account.   A. R. ROGERS

2492. Applications of infra-red spectroscopy. H. W. Thompson (Phys. Chem. Lab., Oxford). *Chem. & Ind.*, 1957, (4), 92–95.—The present state of development of i.r. equipment and technique, both for laboratory and process-control work, is discussed, and possibilities of extending existing methods of analysis are outlined.   G. S. ROBERTS

2493. Systematic errors in spectrometric measurements in a study of fluorescence. C. Chechan, R. Audran and A. Verain. *Chim. Anal.*, 1957, **39** (2), 59–61.—Both the spectroscope and the spectrograph as a means of estimating fluorescence are subject to systematic errors. The distribution of energy in the spectrum of the source is not constant, the dispersion of the prism arrangements commonly used diminishes from short to long wavelengths, and photoreceptors are selective; their sensitivity varies considerably with wavelength in accordance with a specific law for each type. The importance of the last two errors, and means of overcoming them are discussed. Results of examination of a particular "fluorescent" solid by means of a photoelectric spectrometer are considered. It may at least be possible to find a means of identifying specific fluorescent bodies, in spite of these difficulties. The prescription of a particular emulsion or photo-electric cell might be hard to impose. On the other hand, visual observation could be applied only by observers having a definite, normal chromatic sense.   W. J. WRIGHT

2494. The application of X-ray fluorescence to trace analysis. M. B. Cavanagh. [U.S.] Naval Research Lab. Report 4528, April 1955, 4 pp.—The micro-determination of Hf, Nb, Ta, Th and U in iron by X-ray fluorescence is described. Iron and impurities are removed by electro-deposition in mercury and the residual elements are concentrated on mylar film. Each of these elements (5 μg) can be determined in the presence of each other with an accuracy of $\pm 10\%$ of the amount present.   BULL. B.N.F.M.R.A.

2495. Phosphorimetry. A new method of analysis. R. J. Keirs, R. D. Britt, jun., and W. E. Wentworth (Florida State Univ., Tallahassee, Fla., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 202–209.—Phosphorescence can be excited in many organic mol. containing double bonds when a soln. of the material in a suitable solvent is frozen to a rigid glass. The phosphorescence is unique for each mol., being characterised by the mean life-time, frequency, vibrational patterns and the quantum yield, and can be used for qual. identification. By suitably controlling the conditions, and using a resolution phosphoroscope, the quant. analysis of mixtures of compounds can be carried out with a mean error (relative) of $\simeq 10\%$. Use is made of differences in mean life-times and in frequency of the phosphorescence, and also of selective excitation.   J. H. WATON

2496. Thermogravimetric analysis of complex mixtures of hydrates. E. J. Griffith (Monsanto Chem. Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 198–202.—When a suitable rate of heating is found, the use of the thermogravimetric balance allows the water content of each phase of a mixture of hydrates to be determined. The presence of anhyd. salts has no effect. Provided that a phase contains at least 20% of the total water, the average error of the determination of the water in the phase is $\simeq \pm 1\%$. The technique could be adapted to the analysis of the cryst. substances that contain the water in the mixture, if all the phases are completely hydrated before their decomposition.   J. H. WATON

2.—INORGANIC ANALYSIS

2497. Decomposition of minerals by fusion with borax. P. G. Jeffery (Geological Survey of Uganda, P.O. Box 9, Entebbe, Uganda). *Analyst*, 1957, **82**, 66–67.—Fusion with borax in a platinum crucible is recommended for rapid decomposition of oxide minerals, particularly those exhibiting resistance to decomposition, *e.g.*, the oxides of Nb and Ta and those containing Ca and Ti together. By dissolving the melt in dil. HF the advantages of the Lawrence Smith method are retained and the rare earths and Th are separated as insol. fluorides with most of the Ca of such minerals as perovskite, microlite and pyrochlore. The filtrate contains most of the Fe originally present and all the unvolatilised B, together with all the Ti, Nb and Ta. One copious fuming with H_2SO_4 removes all the F and B. Recovery of Nb_2O_5, Ta_2O_5 and TiO_2 after fusion with borax and pptn. with tannic acid was good. The grinding of samples to impalpable powders is not necessary. Bismutotantalite should not be fused with borax in platinum ware.   A. O. JONES

2498. The titration of bivalent metals with the disodium salt of ethylenediaminetetra-acetic acid. J. Haslam, D. C. M. Squirrell and M. Heskins (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *Analyst*, 1957, **82**, 117–120.—The method developed by Schwarzenbach ("*Die Komplexometrische Titration*," Ferdinand Enke Verlag, Stuttgart, 1955, p. 50) based on the measurement of the acid liberated by the interaction of certain bivalent metals (*e.g.*, Cu and Zn) with the disodium salt of EDTA is shown to be unsatisfactory. An alternative form of titration is described in which the bivalent metal is titrated with a standard soln. of the disodium salt of EDTA until the pH of the liquid ceases to alter with further addition of titrant. The titration is made with an automatic titrimeter, and the method is likely to be useful with highly coloured soln. or with metals that form coloured complexes with EDTA.
                                                          A. O. JONES

2499. Developments in the micro vacuum fusion method with particular reference to the determination of oxygen, nitrogen and hydrogen in beryllium, titanium, zirconium, thorium and uranium. E. Booth, F. J. Bryant and A. Parker (U.K. Atomic Energy Authority, Res. Group, Woolwich Outstation, England). *Analyst*, 1957, **82**, 50–61.—The apparatus used is that described by Gregory *et al.* (*Analyst*, 1953, **78**, 414), with certain additions. The manipulation of the apparatus is described and examples are given of the determination of O and H in titanium, in zirconium and its alloys, in thorium (rod and powder), in uranium (rod) and in tantalum. Determinations were successful also with boron, copper, chromium, silicon and steel. Sampling difficulties occur with zirconium sponge. With beryllium, results were less satisfactory and work is still in progress. In the determination of N, results by the vacuum-fusion method were all low in comparison with those obtained by the Kjeldahl procedure, and the method appears to be unreliable for elements that form stable nitrides, particularly titanium, zirconium and thorium.   A. O. JONES

2500. The separation of metals by ion-exchange chromatography. R. N. Golovatýĭ. *Nauk. Zap. L'vivs'k. Univ.*, 1955, **34** (4), 118–124; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,912.—Methods of separation of metals on the surface of cationites and from soln. are given. The possibility is indicated of the individual and group separation of Zn, Cu, Co, Ni and Cd from Fe, Al, Mo and V by ion-exchange chromatography, with an excess of $NaPO_3$ as the complexing agent and aq. NH_3. The selective adsorption of the complex ions in the presence of simple ions is noted. This allows the use of small quantities of adsorbent. For the extraction of Co, Ni, Zn, Cd, Cu and Ag from industrial effluents, they must first be transformed into complex ions. It is established that simple cations adsorbed on the cationite from neutral or acid medium are easily washed out by salt soln. of any concn., while the ammonia-complexed cations require a definite concn. of salt in the regenerating soln. The stability of the complex ammoniates with respect to NaCl soln. is studied. On treating the surface of the metal cationite with aq. NH_3, Fe^{3+}, Cr^{3+} and Al^{3+} lose their cation-exchange ability and may thus be separated from all the cations of the first three analytical groups.
                                                          C. D. KOPKIN

2501. Separation of heavy metals with acid alkyl phosphate and phosphonate resins. J. Kennedy, R. V. Davies and B. K. Robinson (A.E.R.E., Harwell, England). A.E.R.E. Report C/R 1896, 1956, 5 pp.—Retention on a cation-exchange column (diallyl phosphate polymer in acid or sodium form) decreases in the order $UO_2^{2+} > Fe^{3+} > La^{3+} > Cu^{2+}$, Co^{2+}, $Ca^{2+} > Na^+$ from a soln. of their nitrates. Separation of UO_2^{2+} from Ca^{2+}, Co^{2+} and Cu^{2+} is achieved directly on the acid form of the resin, and from Fe^{3+}, Cu^{2+}, Co^{2+} and La^{3+} by total adsorption on the resin as its sodium form followed by leaching with EDTA (disodium salt). Uranyl is recovered by leaching with Na_2CO_3. Separation of UO_2^{2+} from Zr^{4+} and Th^{4+} is not complete.
                                                          D. A. PANTONY

2502. The determination of impurities in alloys and amalgams by amalgam polarography. A. G. Stromberg and A. A. Pȳshkina. *Trudȳ Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 136–141; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,929.—The amalgam dropping electrode is immersed in a soln. of an indifferent electrolyte and the anodic polarographic wave recorded. The advantages of the method are its use for the determination of electronegative impurities in a more electropositive base metal. The method may be used for the analysis of amalgams and of alloys which dissolve in mercury. It may be conveniently used in conjunction with electrolysis. After separation of the metals by electrolysis on a mercury cathode, one metal may be determined in the aq. soln., and another in the amalgam. The amalgams are prepared in special vessels in a current of hydrogen to avoid oxidation. The method has been tested for the determination of Zn in Cd, Cd in Pb, and Pb in Bi. Hundredths of a per cent. of impurity may be determined with a relative error of 3 to 5% in 20 to 30 min.   C. D. KOPKIN

2503. Complexometric titrations (chelatometry). XXII. The volumetric determination of iron, aluminium and titanium in silicates. Notes on the chelatometric determination of calcium and magnesium. V. Patrovský and M. Huka (Centr. Geolog. Inst., Prague). *Coll. Czech. Chem. Commun.*, 1957, **22** (1), 37–42 (in German).—Dissolve 0·5 to 1 g of sample in HCl, add 1 ml of HNO_3 to oxidise Fe, evaporate to dryness and filter off SiO_2 after extraction of the residue. Neutralise the filtrate with aq. NH_3 to the appearance of the brown cloudiness

or colour of basic Fe^{III} salts, and clear the soln. with HCl (one drop). Add hexamine soln. (10%) (10 ml) and warm to between 80° and 90°. Filter off the hydroxides of Fe, Al and Ti, wash them with a 0·5% soln. of the precipitant, then dissolve in the min. quantity of warm HCl (1:1) or H_2SO_4 (1:3). The hydroxides do not dissolve easily in H_2SO_4, but Ti can be directly determined in such soln. colorimetrically with H_2O_2. Make the soln. up to 100 ml. Use 50- or 25-ml aliquots for the determination, and the remainder for determining Ti and for control determinations. Dilute the soln. and determine Fe by titration with 0·1 M EDTA (disodium salt) (I), with sulphosalicylic acid at pH 2 to 3 at 40° to 50°, to a dark-blue colour. With a low content of Fe, it is recommended to work in a small volume and to add more sulphosalicylic acid towards the end-point. After the titration of Fe, add a moderate excess of I soln., adjust the pH to ≃ 4·5 by adding a small excess of Na acetate, and allow to stand for 5 to 10 min. Add a few drops of 0·1% aq. catechol violet soln. If the soln. is blue or green, add more I soln. to a yellow colour. Add hexamine (1 or 2 g) and, with constant stirring, add 5% aq. NH_3 dropwise to a dirty yellow colour. Titrate the excess of I with 0·1 M $CuSO_4$ to a dark-blue colour. The amount of I equivalent to Al plus Ti is thus obtained. The Ti is determined colorimetrically in an aliquot of the soln. Interference is caused by Mn, Co, Ni, Zn, Be and Cr; V^V causes no marked interference, and V^{IV} has a slight effect, which is negligible from small quantities. Borate, phosphate, Ca and Mg do not interfere. The Fe, Al and Ti may be separated from Mn with hexamine, pyridine or Na acetate. The filtrate may then be used for the determination of Mn, Ca and Mg. Determine Mn colorimetrically with formaldoxime (up to 0·2 mg in 50 ml). If Ca is to be determined, Mn must be removed by adding 5% dithiocarbamate soln. Extract the brown-red (or, in the presence of Cu, yellow) cloudiness or ppt. with $CHCl_3$, and after evaporation of the solvent and solution of the residue in HCl, determine Mn complexometrically with catechol violet soln. or Eriochrome black T as indicator. The Cu is held with cyanide. If the ammonium content is not too high, determine Ca with I soln. against murexide; the pH must be at least 11. The ammonium content should be as low as possible. Remove Mn from the soln. with dithiocarbamate, or complex it with triethanolamine. Titration with I soln. in the usual ammoniacal buffer soln. with Eriochrome black T gives Ca plus Mg. In the presence of cyanide or dithiocarbamate it is possible to titrate Mg in 10% NH_4Cl soln. to Eriochrome black T. Addition of dithiocarbamate holds not only Cu, Mn, Ni, Co and Zn, but also traces of Pt picked up from crucibles. The murexide and Eriochrome black T indicators are used in admixture with NaCl (1:100). (This paper was published in Czech in *Chem. Listy*, 1956, **50**, 1108.)   C. D. KOPKIN

2504. Arsenous oxide as a primary standard in the iodimetric analysis of hydrogen peroxide. B. R. Sant (Univ. Benares, India). *Chim. Anal.*, 1957, **39** (2), 53-54.—Substitution of $NaAsO_2$ for $Na_2S_2O_3$ in the iodimetric titration of H_2O_2 has the advantage of permitting the direct usage of As_2O_3 as standard. A 0·1 N soln. of As_2O_3 was prepared by dissolving 4·946 g in conc. NaOH soln., neutralising with 6 N HCl, buffering with 5 g of $NaHCO_3$ and diluting to 1 litre. An aliquot of H_2O_2 soln. was mixed with 20 to 25 ml of 2 N H_2SO_4 and 20 ml of 10% KI soln., and set aside for 10 to

15 min. A buffer soln. of borax (8%) and boric acid (4%) was added to bring the pH to ≃ 9, and the liberated iodine was titrated with the As_2O_3 soln., with starch as indicator. Comparative results with $Na_2S_2O_3$ and As_2O_3 are tabulated for several concn.   W. J. WRIGHT

2505. Chromatographic separations in phenol-methanol-hydrochloric acid solvents, with special reference to the alkali metals. R. J. Magee and J. B. Headridge (King's Buildings, The University, Edinburgh). *Analyst*, 1957, **82**, 95-101.—A phenol-methanol-HCl mixture (57:22·5:20, w/v/v) (I) is used to separate the chlorides of Li and Na, and of K, Rb, Cs and ammonium by downward paper chromatography. The test soln. (0·01 ml) are placed on a strip accommodating four tests. After removal from the tank, the dried papers are sprayed with zinc uranyl acetate to detect the Li and Na by their brilliant green fluorescence in u.v. light, and the bands are compared with standards. For K, Rb, Cs and ammonium the paper is sprayed with ethanol, then immediately with a sodium lead cobaltous hexanitrite reagent (prep. described), dried and compared with standard sets. The bands of K and ammonium are grey, Rb brown, and Cs yellow-brown. The min. amounts detectable (in the presence of 10 μmoles of any other or total of all) are 0·1 μmole of Na, K, Rb and Cs and 0·25 μmole of Li and ammonium. The application of the method to the analysis of rocks containing Rb and Cs is described. With a modification of the mixture I (50:20:30), small amounts of Al, Ga, In, Th, Zn and Ti, Zr and Fe can be separated. For Al, Ga, In, Zn and Fe the reagent is 8-hydroxyquinoline; for Th, KI; for Ti, chromotropic acid; and for Zr, alizarin.   A. O. JONES

2506. The separation of lithium from alkali-metal ions. G. A. Guter and G. S. Hammond (Iowa State Coll., Ames, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 5166-5167.—It is shown that dipivaloylmethane (I) has the property of selectively binding Li^+ under alkaline conditions and it is possible to determine Li in the presence of Na and K. *Procedure*—A soln. containing Li^+ (0·5 N), Na^+ (0·5 N), and K^+ (1·0 N) (1 ml) is shaken with I (0·1 N) (50 ml) in ether for 2 min. (I is prepared by the method of Hauser and Adams, *J. Amer. Chem. Soc.*, 1944, **66**, 1220). An aliquot (25 ml) of the ether soln. is mixed with water (25 ml) and titrated with 0·1 N acid. This estimation is repeated three times more and the combined aq. layers (1-ml aliquots) are re-extracted twice more. The residual aq. soln. (1-ml aliquot) is extracted once more to give a blank reading (corresponding to extracted Na). The blank is subtracted from each of the first four readings and from the mean of the second two. The figure from this mean is added to each of the others and the percentage of Li is calculated. The method gives an accuracy within ± 1%.   C. A. SLATER

2507. New microchemical reaction for the sodium ion. A. N. Sposobnaya. *Sb. Rabot. Stud. Nauch. Ob. Leningr. Tekhnol. Inst. Pishch. Prom.*, 1956, (1), 74-77; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,944.—In the reaction of $K_2H_3P_2O_7$ with Na^+, needle-shaped crystals are formed, which are observed under the microscope ($\times$ 120). The soln. is first treated with N K_2CO_3 to remove heavy-metal and alkaline-earth metal ions. The sensitivity of the reaction is 0·04 $\times 10^{-6}$ g. The limiting dilution is 1 in 25×10^3.   C. D. KOPKIN

2508. Sensitivity of the detection of potassium as its tetraphenylboron salt. A. M. Amin (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1957, **46** (1), 6–8.—The test is best made at pH 5·4 (Na acetate buffer), at which value the limit of detection is 0·09 μg of K^+ and the limit of dilution is 1 in 3.5×10^5. Although both sensitivity and dilution limits decrease with increasing acidity, the test is sufficiently reliable at pH < 1 (*viz*, in 1% HCl) to be used as a spot test. Most other metal ions (except Ag^+ which must be removed initially) do not affect the sensitivity, provided that one drop of a 4% (w/v) soln. of EDTA (disodium salt) is present and that their concn. per drop are in the microgram range. W. J. BAKER

2509. Direct alkalimetry of potassium tetraphenylboron in presence of mercuric chloride. R. Montequi, A. Doadrio and C. Serrano (Inst. "Alonso Barba," Madrid). *Inf. Quim. Anal.*, 1957, **11** (1), 8–12.—Potassium is determined in soln. (0·5 mg of K^+ per ml) by acidification with HCl and pptn. by the gradual addition of Na tetraphenylboron soln. (1·2%). The ppt. is washed, transferred to a flask, treated with aq. sodium mercurichloride (0·5 N in Hg), heated on a water bath and titrated with NaOH soln. (0·05 N) in the presence of methyl red to a stable end-point colour. The presence of acetone (as used in some similar procedures) was disadvantageous. From 1 to 10 mg of K may be determined. L. A. O'NEILL

2510. New method for the gravimetric determination of copper. E. Papafil, M. A. Papafil and D. Furnică. *Anal. Ştiinţ. Univ. "Al. I. Cuza" din Iaşi*, I, 1955, **1** (1–2), 294–300.—An aq. soln. of *o*-nitrobenzaldoxime gives a green basic complex with Cu^{2+}, which is insoluble in water or dil. aq. NH_3 soln., and has the constitution $(C_7H_5O_3N_2)_2 \cdot Cu_2(OH)_2$. The ppt. can either be filtered off, washed with water, ethanol and ether, and weighed, or ignited to CuO. N. E.

2511. Bismuthiol II as an analytical reagent. V. Estimation of silver. Anil Kumar Majumdar and Bhu Ratna Singh (Jadavpur Univ., Calcutta). *Z. anal. Chem.*, 1957, **155** (2), 81–86 (in English).—The reagent (*cf. Anal. Abstr.*, 1957, **4**, 2169) forms a complex with Ag which has the composition $C_8H_5N_2S_3Ag$ and when formed from neutral soln. in the presence of NH_4NO_3 is stable up to 280°. Pptn. of Ag^+ is complete in soln. of HNO_3 of concn. up to 0·2 N; in H_2SO_4, acetic acid or aq. NH_3 up to 1 N; and also in the presence of citrate, tartrate, EDTA (disodium salt) and cyanide. From 0·1 N HNO_3 soln. only elements of the sulphide group are pptd. Other ions, with the exception of Hg^+, Hg^{2+}, Pt^{4+}, Pd^{2+} and Au^{3+}, can be separated with the aid of tartrate, citrate or EDTA (disodium salt) at pH 5 to 9; Pd^{2+} can be masked with cyanide and Au^{3+} with thiosulphate. G. BURGER

2512. Spectrochemical determination of silver in galena. A. Buccheri and J. Galha (Inst. de Pesquisas Tecnol., S. Paulo, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 113–121.—The sample of galena (containing 0·04 to 0·18% of Ag) is powdered and homogenised and mixed with glycerol to a paste. A graphite electrode is used to support the paste. The sample is excited by a 12-kV spark discharge of the Feussner type. Bismuth, introduced in the form of a salt before mixing the sample with glycerol, is used as reference. The coeff. of variation is ±3·1%, and

results demonstrated the method to be as precise as any of the classical methods. Elements such as Zn, As, Sb, Fe, Si, Cu and perhaps Pb may also be determined by this procedure. H. PRITCHARD

2513. Flame-photometric estimation of the alkaline-earth metals in the presence of other metals. K. Ettre and J. Ádám (ForschungsInst. der Fernmeldetech., Budapest). *Z. anal. Chem.*, 1957, **155** (2), 105–114.—Flame-photometer readings for Ba, Sr and Ca are taken at 487·0 mμ, 460·7 mμ and 422·6 mμ, respectively. Although Cu, Ni and Fe emit light in the waveband 420 mμ to 550 mμ, there is negligible interference with the readings for Sr and Ca, but considerable interference with those for Ba. The emissions are additive and correction is made by Freytag's method (readings at two wavelengths). Corrected results are accurate to within ± 4%. The presence of Fe diminishes the emission due to Sr. This effect depends only on the concn. of Fe and correction can be made by estimating Fe at 450 mμ. Zirconium and Al do not emit, but reduce the emission of Ca, Ba and Sr. The effect of Zr on Ba and Sr increases with concn. of Zr to a saturation value. By adding Zr in excess of this value, a factor of 1·9 for Ba or 3·65 for Sr can be applied to give results correct to within ± 4% and ± 6%, respectively. Below the saturation value Zr can be estimated by the magnitude of its effect on Ba or Sr. When Ca, Sr, Ba and Zr are present together, Sr, Ba and Zr can be estimated as described above, and the Ca from a curve showing the effect of Zr on emission due to Ca. Curves and literature references are given for the effect of Al. G. BURGER

2514. Rapid quantitative separation of traces of beryllium. J. Schubert, A. Lindenbaum and W. Westfall (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Chimia*, 1957, **11** (2), 50–51 (in English).—A method of separating micro amounts of Be from minerals and metals, such as copper, is based on the fact that Be forms a strong complex ion with salicylate compounds beginning at about pH 3. Cations of the alkaline earths do not react with salicylates, and cations such as Cu^{2+} and UO_2^{2+} react weakly in the same pH region. The Be plus the foreign cations may be added to a column of a cation-exchange resin, and Be then eluted selectively with > 0·02 M sulphosalicylic or gentisic acid between pH 3 and 4·5; Cu^{2+}, UO_2^{2+} and Ca^{2+} are not removed. At pH 2·7 and above, Be can begin to come off the column, according to the concn. of the eluting agent. After Be is removed, the remaining foreign cations can be removed by one of several eluting agents, such as H_2SO_4 or HCl. W. J. WRIGHT

2515. Acidimetric determination of beryllium with sodium salicylate. V. K. Zolotukhin. *Nauk. Zap. L'vivs'k. Univ.*, 1955, **34**, 115–117; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,822.—To determine Be in neutral and acid media and in basic salts, treat a definite vol. of the beryllium salt soln. with an excess of 0·4 N Na salicylate soln., and neutralise to thymolphthalein with 0·1 N NaOH. Add a 1·25 to 3-fold excess over the theoretical quantity of 0·1 N HCl and a 2 to 3-fold excess of KF soln., neutralised to phenol red (**I**), to a transient orange colour. After 3 to 5 min. titrate the excess of acid with 0·1 N NaOH in the presence of **I**. Best results are obtained with a mol. ratio of $BeSO_4$ to Na salicylate of 1:3·2 and a 0·25-fold excess of HCl. Increase of the excess of the salicylate increases the quantity of HCl required. C. D. KOPKIN

2516. New colour reaction for the calcium ion.
E. P. Markhel'. *Sb. Rabot Stud. Nauch. Ob.
Leningr. Tekhnol. Inst. Pishch. Prom.*, 1956, (1),
78–83; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,956.
—To detect Ca^{2+}, moisten a strip of filter-paper with
$0.1 N$ Fe^{3+} soln., dry it, dip it in $0.6 N$ NaF or KF
soln., dry it, dip it in $0.1 N$ SCN^- soln., and add a
drop of the test soln. In the presence of Ca^{2+} a red
spot is formed. The sensitivity of the reaction is
$0.04 \mu g$, the limiting dilution is 1 in 4×10^5. No
interference is caused by Mg^{2+}, Ba^{2+}, Sr^{2+}, Cl^-, Br^-,
NO_3^- and SO_4^{2-}.   C. D. KOPKIN

**2517. New complexone for titration of calcium in
the presence of magnesium.** R. W. Schmid and
C. N. Reilley (Univ. of N. Carolina, Chapel Hill,
U.S.A.). *Anal. Chem.*, 1957, **29** (2), 264–268.—
When Ca and Mg are titrated together by means of
EDTA (disodium salt) (**I**), with a mercury indicator
electrode to give a potentiometric end-point, no
break is evident between the titration of Ca and
Mg, but a break occurs when both have been
titrated. If 1:2-di-(2-aminoethoxy)ethane-NN′-
tetra-acetic acid (**II**) replaces **I**, then a break
occurs only between the titration of Ca and Mg, but
not at the end. For the estimation of Ca and Mg
in the presence of each other, it is recommended
that Ca be estimated by titration with **II**, and Ca
and Mg together by titration with **I**. The average
error (relative) for a Ca determination is $\pm 0.3\%$
and for Mg $\pm 0.7\%$.   J. H. WATON

**2518. New indicator for complexometric titration
of calcium in presence of magnesium.** G. P.
Hildebrand and C. N. Reilley (Univ. of N. Carolina,
Chapel Hill, U.S.A.). *Anal. Chem.*, 1957, **29** (2),
258–264.—Calcon (the dye C.I. 202) forms a 1:1
complex with Ca, and is suitable for the complexo-
metric titration of Ca in the presence of Mg at pH
12·5. The colour change from pink red to blue is
sharp. The indicator soln. ($0.2 g$ of Calcon in
50 ml of methanol) is stable for at least five months.
The stability constants of the Ca, Mg and Zn
complexes are $10^{5\cdot6}$, $10^{7\cdot6}$ and $10^{12\cdot5}$, respectively;
Sr and Ba give very weak complexes if any.
        J. H. WATON

**2519. Determination of calcium ions by flame-
photometric titration.** L. Erdey and G. Svehla
(Inst. für Allgemeine Chem., Tech. Univ., Budapest,
Hungary). *Z. anal. Chem.*, 1957, **154** (6), 406–413.
—Concn. of Ca^{2+} in the range 0·001 to 0·1 M have
been determined with an accuracy of $\pm 2\%$ by
flame-photometric titration with standard H_3PO_4
soln. A Zeiss flame photometer with a modified
atomiser was used to follow the fall in concn. of
Ca^{2+}. A graph relating galvanometer reading and
volume of H_3PO_4 added showed a distinct change of
slope at the equivalence point, especially when a
correction was applied for dilution. A. R. ROGERS

**2520. Filtration - precipitation separation of
barium-140 from lanthanum-140.** R. W. Perkins
(General Electric Co., Richland, Wash., U.S.A.). *Anal.
Chem.*, 1957, **29** (1), 152–153.—Carrier-free ^{140}Ba
can be rapidly separated from its daughter ^{140}La by
filtering their soln. through an ion-exchange resin
in the free-base form. The ^{140}La is pptd. on the
resin and the ^{140}Ba passes through in the eluate.
The ^{140}La may be eluted with dilute HNO_3. The
procedure is very rapid and may be repeated on the
same exchange bed an indefinite number of times.
Both separated elements were shown to be radio-
chemically pure by decay measurements.
        L. S. ADLER

**2521. Flame-spectrophotometric analysis of
glasses. II. Calcium, magnesium and barium, in-
cluding the alkalis.** J. P. Williams and P. B. Adams
(Corning Glass Works). *J. Amer. Ceram. Soc.*, 1956,
39 (10), 351–357.—Details of the methods with a
Beckman DU spectrophotometer are given. Since
Al, Fe, Ti, P and Zr interfere, they must be removed
by pptn. with aq. NH_3. The results agreed to
within approx. $\pm 0.15\%$ with those obtained by
wet chemical analysis.   J. A. SUGDEN

**2522. The rapid determination of the alkaline-earth
metals in barium glass.** L. I. Panteleeva and A. A.
Zan'ko. *Nauch. Zap. L'vovsk. Politekhn. Inst.*,
1955, (29), 101–108; *Ref. Zhur., Khim.*, 1956, No.
65,268.—Fuse the glass with 2 pt. of Na_2CO_3 and
7 pt. of NaOH in an iron crucible. Leach the melt
by boiling with water, and filter off the insol.
residue, containing the alkaline-earth metals (partly
as silicates) and sesquioxides, after standing in the
warm. Wash the residue with hot water, treat the
residue and filter-paper with conc. HCl (10 ml), add
to the mixture 10 ml of a 1% gelatin soln., warm for
10 min. on the water bath, filter off the pptd. SiO_2
and wash it with hot water. Precipitate with aq.
NH_3 the hydroxides of the tervalent metals, and re-
precipitate after dissolving in HCl (1:1). Combine
the filtrates from both pptn., make up to a definite
vol., and determine Ca, Ba and Mg in separate
aliquots. For Ca, first remove Ba and Sr with a
calculated quantity of 0·1 N H_2SO_4 (a 20% excess
does not interfere), evaporate to dryness, treat with
HCl (1:1), dilute with water and precipitate Ca
as oxalate and determine with $KMnO_4$ in the
normal way. For Ba, add ammonium acetate and
precipitate Ba with 3% $(NH_4)_2CrO_4$. Filter off the
ppt., wash it with 0·6% ammonium acetate soln.,
dissolve it in HCl (1:1) and determine chromate
iodimetrically. For Mg, add ammonium salts and
precipitate from the boiling soln. with a 2% alco-
holic soln. of 8-hydroxyquinoline. Allow the ppt. to
settle while on a water bath, filter, wash off excess
of reagent, and finish the determination with
bromate and KI in the normal way. The results
of the determination of the alkaline-earth metals by
the rapid and the classical methods agree to within
0·4 to 2%.   C. D. KOPKIN

**2523. Determination of zinc in minerals and
metallurgical products by the sublimation procedure.**
W. Geilmann, R. Neeb and H. Eschnauer (Inst. für
anorg. und anal. Chem., Univ., Mainz). *Z. anal.
Chem.*, 1957, **154** (6), 418–430.—A procedure which
involves sublimation in a stream of H at 1100° is
recommended for the rapid determination of Zn in
pyrites and similar material (*cf. Anal. Abstr.*, 1955,
2, 2057). The concn. of Zn^{2+} in a soln. of the
sublimate is determined by potentiometric titration
with ferrocyanide. Modifications are described
which serve to eliminate interference by other
volatile metals.   A. R. ROGERS

**2524. A new sensitive and selective spot test for
mercury.** I. Kraljić and M. Mate (The Univ.,
Zagreb, Yugoslavia). *Croat. Chem. Acta*, 1956, **28**
(4), 273–277 (in English).—The test is based on the
catalytic effect of Hg^{2+} on the decomposition of
$Fe(CN)_6^{4-}$ in the presence of nitrosobenzene (*cf.
Anal. Abstr.*, 1957, **4**, 2541) whereby the pink or violet
water-sol. $[Fe(CN)_5.NO.C_6H_5]^{3-}$ is formed. The
sensitivity is $0.002 \mu g$ of Hg (in 0·05 ml) or a
limiting concn. of 1 in 25×10^6. *Procedure*—To
one drop of sample soln. on a spot-plate, or in a test-
tube, add one drop of a mixture (1 + 9) of acetate

buffer and saturated aq. nitrosobenzene, followed by one drop of a 0·5% soln. of $K_4Fe(CN)_6.3H_2O$. Warm to 60°, adding another drop or two of nitrosobenzene if a spot-plate is used. Sufficient buffer should be present to maintain the pH at 4·1, and for concn. of $Hg < 10^{-6} M$ a blank should be run simultaneously. Silver ($> 2 \times 10^{-5} M$) and Au ($> 10^{-5} M$) also give this reaction; other interfering cations (Fe^{3+}, Cu^{2+}, UO_2^{2+}) can be suitably eliminated. Iodide in concn. $> 10^{-4} M$ interferes seriously, but most other anions in concn. up to $\simeq 0·01 M$ can be tolerated.   W. J. BAKER

2525. Amperometric titration of mercury(II) with tetraphenylarsonium chloride. O. Menis, R. G. Ball and D. L. Manning (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 245–248.—Mercury in the range 0·025 to 2·3 mg is estimated with a precision of $\pm 3\%$ when 0·4 M HNO_3 is used as supporting electrolyte. The fixed titration potential can be varied between 0 and –0·6 V (*vs.* the S.C.E.). The presence of a small excess of other ions should not cause interference.   J. H. WATON

2526. Acidimetry - alkalimetry possibilities with mercuric salts. R. Montequi, A. Doadrio and M. Fernández Santiso (Inst. "Alonso Barba," Madrid). *Inf. Quím. Anal.*, 1957, **11** (1), 1–7.—Mercuric chloride (0·1 N) can be determined by boiling with acetone ($\simeq 50\%$ on final titrated solution) to form a complex, and titration with NaOH (0·1 N) to phenolphthalein. Similarly, $HgCl_2$ may be used to standardise alkali soln. Urea, used in place of acetone, also gives good results provided that it is present in sufficient amount. To determine $HgSO_4$, NaCl is added and the initial acidity titrated, with bromocresol green as indicator. Acetone is then added to form the complex and the mercury salt is determined by titrating the heated mixture to phenolphthalein.   L. A. O'NEILL

2527. The use of zincon in the absorptiometric determination of mercury. A. G. Morris (Hopkin & Williams Ltd., Chadwell Heath, Essex, England). *Analyst*, 1957, **82**, 34–37.—Zincon (2-carboxy-2'-hydroxy-5'-sulphoformazylbenzene) gives a stable and sensitive blue colour reaction with Hg^{2+}. A suitable aliquot of the soln. containing 100 to 400 μg of Hg^{2+} is adjusted to pH 7·2 and is mixed with 3 ml of aq. zincon soln. (0·13 g dissolved in 2 ml of N NaOH and diluted to 100 ml) and the mixture is diluted to 50 ml with a buffer soln. of pH 7·2. The extinction of the liquid is measured at 600 mμ against a reagent - buffer blank and the content of Hg^{2+} is ascertained from a calibration graph. The determination may also be made visually by adjusting the pH of the sample soln. to 7·2, diluting the soln to 50 ml in a Nessler tube with the buffer soln., adding 0·25 ml of a tenfold dilution of the zincon reagent and comparing the colour with that of a control containing identical amounts of buffer soln. and reagent. The extent of interference by other ions is discussed.
A. O. JONES

2528. A new analytical separation technique using ion-exchange membranes and its application to the determination of boron in sodium metal. D. Logie (I.C.I. Ltd., Widnes Lab., Lancs., England). *Chem. & Ind.*, 1957, (8), 225–227.—The complete method for the determination of B in sodium metal involves conversion of the metal to a soln. of the hydroxide, electrolysis in the anode compartment of an electro-migration cell fitted with a cation-

exchange membrane, purification of the anode liquor with a small cation-exchange column, evaporation of the alkaline eluate and colour development. Details are given of a suitable two-compartment electro-migration cell constructed in Perspex. If 5 g of sample is used, the theoretical limit of the method should be about 0·05 p.p.m. of B. The procedure has been applied to other problems and is particularly useful when the concn. of solute in a sample soln. is greater than can be conveniently handled by a conventional ion-exchange column.   K. A. PROCTOR

2529. The determination of traces of boron in nickel. R. C. Chirnside, H. J. Cluley and P. M. C. Proffitt (The General Electric Co. Ltd., Wembley, Middx., England). *Analyst*, 1957, **82**, 18–24.—The method was designed to determine B in nickel sheet used in thermionic valves. A weighed strip of the sample forms the anode of an electrolytic cell, with Hg in a platinum crucible as the cathode. The electrolyte in the crucible is 0·02 N H_2SO_4. As electrolysis with a current of 3 amp. proceeds, preferential attack occurs at the surface of the electrolyte and the immersed portion of the strip ultimately breaks off. The strip is then removed for weighing and is replaced by a platinum strip and electrolysis is continued until solution of any fragments of Ni and their deposition into the Hg is complete. The electrolyte in a platinum dish is evaporated with a glycerol - NaOH reagent and, after removal of the glycerol by heat, is treated according to a specified procedure with a curcumin - HCl reagent. After removal of the HCl by evaporation, the colour is extracted with ethanol and the extinction of the extract is measured at 550 mμ and related to the content of B by means of a calibration graph.   A. O. JONES

2530. Estimation of boron in enamels and glazes. J. Trentelman and A. van Velthuijsen [Ferro Enamels (Holland) N.V., van Helmontstraat 22, Rotterdam]. *Chem. Weekbl.*, 1957, **53** (11), 117–121.—Methods of estimating boron are reviewed. Because of the number of interfering elements that occur in enamels and glazes, separation as methyl borate by distillation is preferred. Apparatus is described in which methyl borate is continuously distilled into an anion-exchange column (Dowex-2, OH form); the boric acid is retained and the methanol is returned to the flask. The apparatus consists of a three-necked flask, with a stirrer, an exit tube to a condenser leading into the top of the ion-exchange column and a return tube from the bottom of the column. The flask is heated on a glycerol - water bath (115°). The sample (0·5 to 1 g) is heated with NaOH pellets (5 g) in a nickel crucible and transferred with the minimum amount of water to the flask, together with a mixture of H_2SO_4 (conc., 20 ml) and 75 ml of methanol. After distillation (approx. 2 hr.), the boric acid is washed out of the column with dil. HCl and titrated. Addition of sodium aluminate prevents interference by F; other elements in glazes do not interfere.   G. BURGER

2531. Acidimetric determination of boric acid with the aid of sorbitol solution. W. Horsch (Pharm. Inst., Karl Marx Univ., Leipzig). *Pharm. Zentralh.*, 1957, **96** (1), 14–15.—Sorbitol may be used instead of glycerol in the titration of boric acid with alkali; the apparent dissociation constant of the sorbitol - boric acid complex is $1·91 \times 10^{-5}$ at 18°. The end-point is sharper than if glycerol is used.
A. R. ROGERS

2532. The effect of pH on the ferri - ferro indicator system in the determination of aluminium by the fluoride method. V. M. Tarayan and E. N. Ovsepyan *Nauch. Tr. Erevansk. Univ.*, 1956, **53**, 75–83; *Ref. Zhur., Khim.*, 1956, Abstr. No. 58,411.—When the pH of the solution being titrated in the potentiometric determination of Al^{3+} with the indicator system Fe^{2+} - Fe^{3+} is 2·2 to 2·5 there is a drop of potential (DP) at the equivalence point; the equivalence point is attained when the pH of the solution being titrated is 3·2 to 4·0. The DP in the titration with a Fe^{2+} - Fe^{3+} electrode or with a quinhydrone electrode is observed at the same point. It was established that the initial value of pH of the soln. being titrated must be 3·0 to 3·1, as at pH $> 3·2$ the results of the determination of Al have started to fall. Premature DP was provoked by the hydrolysis of Fe^{3+} occurring in consequence of reduction in acidity of the soln. being titrated and by the presence of basic salts of Al. It is recommended that the pH of the soln. being titrated be established by the indicator Tropaeolin OO. G. BREWER

2533. Chemical analysis of a mixture of aluminium and iron hydroxides by means of autoclaving and electron diffraction. S. Yamaguchi (Sci. Res. Inst., Ltd., Hongo, Tokyo). *Z. anal. Chem.*, 1957, **155** (1), 21–22.—A mixture of $Al(OH)_3$ and $Fe(OH)_3$, prepared by pptn. with aq. NH_3, was dissolved in dil. HCl, heated slowly to 180° in an autoclave and slowly cooled to room temp. Sufficient aq. NH_3 was then added to complete the pptn. of the Al, and the mixed ppt. was autoclaved with pure water. The resulting mixture showed the characteristic electron diffraction pattern of böhmite. After heating the mixture to 800° in air, the pattern corresponding to γ-Fe_2O_3 was obtained. This procedure thus allows the mixture to be qualitatively analysed. G. BURGER

2534. Quantitative spectrochemical determination of the main elements aluminium and silicon in silicate rocks. F. Hegemann, H. Kostyra and C. von Sybel (Tech. Hochschule, München). *Ber. dtsch. keram. Ges.*, 1956, **33** (9), 283–290.—The aluminium content of granite was determined with a spectroscopic sample mixed with graphite (1:5), with the lines Ni 3050·8 A and Al 3092·7 A. The calibration was provided by the addition of known amounts of Al_2O_3 to a granite low in this oxide. The presence of up to 3% of alkali did not affect the method, which had an accuracy within ± 1·5%. A similar method applied to Si (Co 3995·31 A - Si 2156·12 A) was successful for contents of SiO_2 up to 70%, but above this value it was necessary to mix the sample with Cu (1:40) in order to prevent errors due to the self-adsorption of the Si. J. A. SUGDEN

2535. Rapid analysis of bauxites. A. Vilas (Pretoria Portland Cement, Orkney, S. Africa). *An. Real Soc. Esp. Fis. Quím.*, B, 1956, **52** (12), 767–768.—The finely powdered sample (1000 g) is heated with $CaCO_3$ (4000 g) and the loss in wt. is determined. A weighed amount (1 g) of the calcined mixture is treated with NH_4Cl (1 g) and conc. HCl (10 ml), heated on a steam bath, then filtered, and the ppt. is washed, calcined and weighed. Silica is eliminated from the ppt. with HF and H_2SO_4 to leave an insol. residue, and Al, Fe, Ti, Ca and Mg are determined in the filtrate. L. A. O'NEILL

2536. Bismuthiol II as an analytical reagent. VI. Estimation of thallium (I). Anil Kumar Majumdar and Bhu Ratna Singh (Jadavpur Univ., Calcutta).

Z. anal. Chem., 1957, **155** (2), 86–90 (in English).— Bismuthiol II (*cf. Anal. Abstr.*, 1957, **4**, 2169) forms a yellow complex with Tl^+ with the composition $C_8H_7N_3S_3Tl$, which is stable up to 250° and in the presence of H_2SO_4, HNO_3, NaOH and KOH up to concn. of 0·1 N, and HCl, acetic acid and aq. NH_3 up to 1 N, and in the presence of EDTA (disodium salt), cyanide, citrate and tartrate. Unlike other bismuthiol complexes, the thallous complex is more soluble in hot water, especially in the presence of EDTA (disodium salt). The pptn. is carried out with an 8 to 10-ml excess of reagent at 50° to 60° and the product is cooled in ice to 10° before filtration. The ppt. is washed with ice-cold water. By adjustment of pH and the use of masking agents, Tl can be separated from almost all other ions. G. BURGER

2537. Conductimetric precipitation titration of thallium (I) with sodium tetraphenylboron. W. W. Wendlandt (Texas Technol. Coll., Lubbock, U.S.A.). *Chemist Analyst*, 1957, **46** (1), 8.—From 10 to 20 mg of thallium (*e.g.*, in 5 to 10 ml of 0·008 M $TlNO_3$) can be titrated conductimetrically at 25° to 27° during the pptn. of $TlB(C_6H_5)_4$ with 0·003 M $NaB(C_6H_5)_4$ in dil. acetic acid or neutral soln. The end-point is sharp and, provided that a correction is made for dilution, the accuracy is high. W. J. BAKER

2538. Determination of rare-earth elements and thorium in magnesium with photo-electric recording spectrometer. E. J. Hunemorder and T. M. Hess (Dow Chem. Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 236–238.—Thorium and the rare earths Ce, La, Nd and Pr are determined spectroscopically; a Mg line is used as an internal standard. Although the presence of other alloying elements may cause interference, the errors are eliminated by the method of calibration. J. H. WATON

2539. Separation of the lanthanides by ion exchange with α-hydroxyisobutyric acid. G. R. Choppin and R. J. Silva (Univ. of Calif., Berkeley, U.S.A.). *J. Inorg. Nuclear Chem.*, 1956, **3** (2), 153–154.—By using Dowex-50 X12 (400 mesh) it has been shown that α-hydroxyisobutyric acid (0·3 M) is a superior eluent to EDTA (0·026 M), with respect to flow rate, and to citric and lactic acids with respect to separation factor. The possibility of dimeric diester formation with α-hydroxycarboxylic acids is considered. G. J. HUNTER

2540. Vacuum-fusion determination of oxygen and nitrogen in lanthanum. D. T. Peterson and D. J. Beerntsen (Inst. for Atomic Res., Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 254–257.—By using a nickel bath in the vacuum-fusion analysis of lanthanum, good results are obtained for O and N. The CO and N gases produced are analysed by a mass spectrograph. The recovery of O at 1900° averages only 90·9 ± 1·7%, a consistent loss of $\simeq$ 9% probably being due to adsorption by the vaporised Ni condensed on the upper walls of the furnace tube. The lanthanum samples are dropped into the bath at 1300°, and the temp. is raised to 1900°; most of the N is liberated at 1600°. J. H. WATON

2541. Photometric determination of micro amounts of cyanides. I. Kraljić and M. Mate (The Univ., Zagreb, Yugoslavia). *Croat. Chem. Acta*, 1956, **28** (4), 249–254 (in English).—The

catalytic action of Hg^{2+} on the reaction between $K_4Fe(CN)_6$ and nitrosobenzene is strongly inhibited by even small concn. of CN^-. By establishing optimum conditions for this inhibitory effect, photometric micro-determinations of CN^- concn. from 10^{-5} to 10^{-4} M can be made by measuring the extinction of the violet intermediate product $[Fe(CN)_5NOC_6H_5]^{3-}$. *Procedure*—To an aliquot of the sample soln. add 5 ml of a mixture of freshly prepared soln. of nitrosobenzene, $HgCl_2$ and acetate buffer; then add 5 ml of a 0·21% (w/v) aq. soln. of $K_4Fe(CN)_6.3H_2O$ and make up the vol. to 25 ml. Exactly 20 min. afterwards measure the extinction of the soln. at 528 mμ (green filter) against H_2O as reference standard. A blank should also be run. Subdued light and a const. temp. of 20° should be maintained throughout the experiment. The reagent soln. are prepared so that the following concn. obtain in the final soln.—$HgCl_2$, 40×10^{-6} M; $K_4Fe(CN)_6.3H_2O$, 8×10^{-4} M, nitrosobenzene, 6×10^{-4} M; and acetate buffer (pH 6·2), 4×10^{-2} M. The coeff. of variation is 1 to 6% for CN^- concn. of 1 to 8×10^{-5} M.   W. J. BAKER

2542. Volumetric determination of cyanide and nickel with resacetophenone oxime as an indicator. K. S. Bhatki (Atomic Energy Estab., 414A Cadell Rd., Bombay, India). *Analyst*, 1957, **82**, 24–26.—Potassium cyanide soln. can be titrated with standard $NiSO_4$ or $NiCl_2$ soln., with resacetophenone oxime (2% in 40% ethanol) as internal indicator. The pH ($> 6·2$ and $< 11·0$) is adjusted by addition of Na acetate. At the end-point a greenish-yellow ppt. or turbidity indicates excess of Ni over that required to form the complex. The determination of Ni can also be made by adding Na_2CO_3 soln. until a slight turbidity forms, dispersing this with acetic acid, adding Na acetate and an excess of standard KCN soln. and back-titrating the excess with a standard soln. of Ni. The method is not applicable in the presence of Cu, Co, Zn and certain other metals forming complex cyanides.   A. O. JONES

2543. Rapid method for the determination of silicon in ferrosilicon. G. Hirschfeld (Lab. de Materias Primas, Cia. Siderúrgica Nac., Volta Redonda, Rio de Janeiro, Brasil). *An. Ass. Brasil. Quím.*, 1953, [1956], **12** (1), 25–28.—This method is based on the direct fluorination of the ferrosilicon, followed by the determination of metals in the residue, and obtaining the silicon by difference. The method is empirical, but is useful in routine analysis, since the time taken is about 2·5 hr. as against 12 hr. by the standard method.   H. PRITCHARD

2544. Determination of "free silica" with phosphoric acid. B. Brehler (Mineralogical Inst., Univ. Marburg, Germany). *Ber. dtsch. keram. Ges.*, 1956, **33** (10), 329–331.—It is shown that the method of determining the total free SiO_2 of a silicate mixture by digestion with a warm solution of H_3PO_4 to dissolve the silicates (*Ibid.*, 1954, **31**, 402) is unreliable because amorphous SiO_2 and part of disordered tridymite and cristobalite crystals are also soluble.   J. A. SUGDEN

2545. The determination of free silica (quartz) in rocks and mine dusts. L. G. Shchekaturina, V. P. Kondratova and V. I. Petrashen'. *Tr. Novocherkas. Politekhn. Inst.*, 1955, **31**, 79–85; *Ref. Zhur., Khim.*, 1956, Abstr. No. 58,456.—On checking the determination of free SiO_2 (quartz) as H_2SiF_6, as proposed by Gurvits and Podgaïts [*Zavod. Lab.*, 1948, (8), 935], high results were obtained. The method proposed by Danil'chenko and Repa

[*Steklo i Keramika*, 1950, (8), 10] for the determination of free SiO_2 in glass as H_2SiF_6 was used with some modification for the determination of free SiO_2 (quartz) in rocks. Satisfactory results were obtained on testing the method with synthetic mixtures.   G. BREWER

2546. Polarographic determination of tin in the presence of tungsten. Yen-Hwa Hu and Shu-Yin Shun (Chem. Lab., Geological Bureau of Eastern China). *Acta Chim. Sinica*, 1956, **22**, 112–116.—For this determination, a supporting electrolyte of $5 \pm 0·5$ N HCl is recommended, and wave-height measurements were stable at 4·5 to 6·0 N HCl. In 6 N, 8 N and 10 N HCl, the half-wave potentials of W were $-0·71$ V, $-0·65$ V and $-0·61$ V vs. the S.C.E., respectively, all of them being virtually coincident with those of the wave due to Sn. In $5 \pm 0·5$ N HCl media, much of the tungstic acid was pptd. and the half-wave potential of traces of tungstic acid remaining in soln. shifted to a more negative value of $-0·75$ V vs. the S.C.E., while that of Sn in the same media remained at $-0·58$ V. The interference of W thus became negligible.
                    S. H. YUEN

2547. The polarographic determination of tin in hydrogen peroxide after use of a cation-exchange resin. G. F. Reynolds (Min. of Supply, Station Approach Buildings, Kidbrooke, London). *Analyst*, 1957, **82**, 46–50.—Tin, present in conc. H_2O_2 as a stabiliser (usually as Na_2SnO_3), is separated from the bulk of the H_2O_2 by means of a cation-exchange resin column (Zeo-Karb 225). An acidified aliquot of the sample and another acidified aliquot containing a standard amount of Sn are each passed through a column which, after being washed with dil. H_2SO_4 and water, is eluted with 5 M HCl. Residual H_2O_2 in the eluate is removed by passing in SO_2 and the excess of this is removed by boiling. After adjustment of the liquids to a definite vol. their polarograms are recorded with the mercury-pool anode. The step occurs at $-0·46$ V and the concn. of Sn is calculated from the step heights of the two soln. The relationship between step height and concn. of Sn is linear up to 15 μg of Sn per ml with columns of the specified dimensions. For higher concn. longer columns are required.
                    A. O. JONES

2548. Bismuthiol II as an analytical reagent. II. Estimation of lead. Anil Kumar Majumdar and Bhu Ratna Singh (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1957, **154** (6), 413–417 (in English).—A simple, rapid and accurate method is given for the determination of Pb^{2+} by pptn. as the complex with bismuthiol II (*cf. Anal. Abstr.*, 1957, **4**, 2169). Oxidising agents should preferably be absent, since they cause decomposition of excess of reagent. Relatively large amounts of Bi^{3+}, Cu^{2+} or Sn^{2+} interfere, but most other metal ions either do not interfere or are easily masked. *Procedure*—Acidify the soln. (containing $\simeq$ 50 mg of Pb) and add NH_4NO_3 (1 to 2 g). Dilute to 125 ml, heat to 70° or 80° and slowly add an excess of bismuthiol II reagent. Digest for a few minutes, filter hot through a sintered glass or Gooch crucible and wash with hot water. Dry at 110° for 1 hr. and weigh as $Pb(C_8H_5N_2S_3)_2$. In the presence of interfering ions, adjust to an appropriate pH, add tartrate or cyanide and allow the ppt. to digest for $\ngtr$ 1 hr. before filtration. If the soln. is strongly acid (*e.g.*, 0·1 N HNO_3), the temperature during pptn. must be kept between 50° and 60°.
                    A. R. ROGERS

2549. Rapid barium chromate method for the determination of lead in ores. G. V. Rozovskaya. *Sb. Nauch.-Tekhn. Inform. Min. Geol. i Okhranȳ Nedr*, 1955, (1), 125; *Ref. Zhur., Khim.*, 1956, Abstr. No. 68,690.—This method for the vol. determination of Pb is based on the titration of CrO_4^{2-} with thiosulphate after pptn. of $PbCrO_4$ from a soln. containing HNO_3. Decompose the ore with HCl in the presence of excess of $BaCl_2$, which will combine with any SO_4^{2-} present. Under these conditions, the formation of a ppt. of the double sulphate of Ba and Pb is precluded. The use of HNO_3 and $BaCl_2$ allows various lead ores to be analysed. The accelerated $BaCl_2$ - chromate method gives satisfactory results in the determination of $> 0.1\%$ of Pb in barium-containing sulphide and oxide ores. The simultaneous determination of ten samples takes 10 to 12 hr.   C. D. KOPKIN

2550. Isotopic analysis of tetramethyl-lead. G. L. Bate, D. S. Miller and J. L. Kulp (Lamont Geological Observatory, Columbia Univ., Palisades, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 84–88.—The use of tetramethyl-lead vapour for the isotopic determination of Pb has been adapted for geological studies, and experiments on the reproducibility of the method, with different spectrometers, sources and spectra, are reported. Two 6-in. mass spectrometers were used with slightly differing sources. The lead spectra in the Pb^+ and $Pb(CH_3)_3^+$ regions were analysed; identical results could be obtained. The $Pb(CH_3)_3^+$ spectrum was used for preference because a slightly better reproducibility was obtained. Within experimental error, the analyses from both mass spectrometers were in agreement. The average reproducibility on duplicate runs was 0.6, 0.4, 0.4 and 0.2% for ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, respectively. An interlaboratory comparison showed agreement generally to within 0.5% for the heavier isotopes, and to about 1% for ^{204}Pb.
                                        L. S. ADLER

2551. The amperometric determination of lead, copper and zinc. A. I. Kostromin. *Uch. Zap. Kazansk. Univ.*, 1956, **116** (1), 179–182; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,954.—Anthranilic acid is used in the amperometric determination of small quantities of Pb, Cu and Zn. The normal visual apparatus, with a dropping-mercury electrode and mirror galvanometer, is used. As a background soln. for Cu and Pb, Na acetate and $NaNO_3$ are used, and for Zn, only $NaNO_3$. The titration of Pb and Cu may be carried out at pH 3.0 to 7.0, and of Zn at pH 4.2 to 5.6. To accelerate the pptn. of Zn, about a quarter of its vol. of ethanol is added to the soln. The possibility is indicated of titrating Cu in the presence of Zn.   C. D. KOPKIN

2552. Polarographic determination of titanium in minerals. Yen-Hwa Hu and Chin-Ching Yang (Chem. Lab., Geological Bureau of Eastern China). *Acta Chim. Sinica*, 1956, **22**, 117–122.—In the modified method described, the supporting electrolyte was $0.5 M H_2SO_4$ - $0.5 M$ tartaric acid. Serious interference due to Cu^{2+} and Fe^{3+} was reduced by adding iron powder (0.2 to 0.5 g per test). The presence of fluoride and vanadate had no ill effect, but molybdate must be absent. Applied to copper, lead, zinc and titanium - iron ores, the proposed method gave results in good agreement with those by a hydrogen peroxide colorimetric method.
                                        S. H. YUEN

2553. Studies of gallic acid complexes with metals and their analytical applications. III. Spectrophotometric estimation of gallic acid [in the determination of titanium]. V. T. Athavale, C. Venkateswarlu and M. S. Das (Atomic Energy Estab., Bombay). *Proc. Indian Acad. Sci.*, 1956, **44** (4), 241–246.—Study of the influence of tartrate, oxalate and citrate ions on the Ti - gallic acid system (TiO_2 in excess) shows that the oxalate and citrate ions interfere seriously with the formation of the coloured complex. With tartrate, max. colour development is attained when the amount of ammonium tartrate is 20 to 28 times (w/w) that of the TiO_2. A spectrophotometric method is described for the estimation of gallic acid over a wide concn. range (up to 10 mg in a total vol. of 50 ml).   I. JONES

2554. Pyrohydrolytic determination of chloride in titanium sponge. A. R. Gahler and G. Porter (Electro Metallurgical Co., Niagara Falls, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 296–298.—Quantitative recovery of Cl^- occurs when the sample is subjected to pyrohydrolysis for 30 min. at 1000° in a nickel or quartz apparatus. The Cl^- in the condensate are determined volumetrically by the Volhard method. The pyrohydrolytic procedure is especially useful for samples that contain $< 0.05\%$ of Cl^-. The whole analysis can be performed in $\not> 45$ min.   J. H. WATON

2555. Determination of titanium dioxide in rutile. J. J. Nogueira, jun. (Inst. de Pesquisas Tecnol., S. Paulo, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 123–125.—After fusion with $KHSO_4$, the sample is dissolved in HCl, the soln. is diluted with water, and neutralised (to methyl orange) with KOH soln. A slight excess of KOH soln. and a little water are added, and any Al present is thus retained in solution as aluminate, while orthotitanic acid and $Fe(OH)_3$ are pptd. The ppt. is dissolved in HCl, the soln. is diluted with water, $Na_2S_2O_3$ soln. is added, and the mixture is boiled. The ferric and titanic salts are thus reduced, and the Ti is pptd. as H_2TiO_3, which is filtered off and calcined and weighed as TiO_2.   H. PRITCHARD

2556. The acid - alkalimetric determination of zirconium and titanium. A. S. Molotkova and V. K. Zolotukhin. *Nauk. Zap. L'vivs'k. Univ.*, 1955, **34**, 125–133; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,830.—Determine Zr in its salts by titration with NaOH in the presence of salts of tartaric, citric and salicylic acids (with concn. of soln. of Zr $\not< 0.1$ N), or in their absence (concn. $\not> 0.025 N$). With excess of anions of the hydroxy acids, even large amounts of KNO_3 and K_2SO_4 exert no influence; cations that react with caustic alkali interfere. Determine Zr in basic salts by the total basicity of soln. of the salt and by the quantity of alkali used in its neutralisation, the basicity being determined on the basis of the reaction—

$$ZrO^{2+} + 6F^- + H_2O \rightarrow ZrF_6^{2-} + 2OH^-.$$
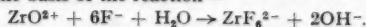
In neutral tartrate soln. Zr cannot be determined by the KF method; in salicylate soln. the error is $\simeq 0.8\%$. Titanium cannot be determined by the described method, since the fluoride complexes of Zr are more stable with reference to alkali than the fluoride complexes of Ti.   C. D. KOPKIN

2557. The separation of zirconium and protactinium by an anion-exchanger column. S. Kahn and D. E. Hawkinson (Tracerlab. Inc., Western Div.,

Richmond, Calif., U.S.A.). *J. Inorg. Nuclear Chem.*, 1956, **3** (2), 155–156.—By using ^{231}Pa and ^{95}Zr the distribution coefficients have been determined for these elements on Dowex-1 X10, 200 to 400 mesh, in 2 to 11 N HCl.   G. J. HUNTER

2558. Quantitative separation of zirconium from iron and nickel by ion-exchange chromatography. I. P. Alimarin, T. A. Belyavskaya and N. M. Rostotskaya. *Vest. Moskov. Univ.*, 1956, (3), 67–71; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,974.—Dilute the soln., containing Zr, Fe and Ni, to 50 ml and at pH $\simeq 1 \cdot 95$ pass it through a column (height 18 cm, diam. 0·6 cm) of cationite SBS (NH$_4$ form), at a rate of 2 ml per min. Collect the eluate, pass through the column 75 ml of 5% ammonium carbonate soln., add this to the main soln., boil out CO$_2$ after adding HCl, and determine Zr. For the removal of the cations of bivalent elements which form complex ammoniates, add a 20% soln. of ammonium carbonate to 20 to 30 ml of the soln. till the ppt. dissolves, plus a 10 to 15-ml excess, pass through the column and wash the column with 50 ml of a 5% soln. of ammonium carbonate. After removal of CO$_2$, determine Zr. From 98·73 to 100% of the Zr is extracted. The method may be used not only for the separation of Zr from Fe and Ni, but also from other bi- and ter-valent elements that do not form complex anions with CO$_3^{2-}$.   C. D. KOPKIN

2559. Determination of iron, titanium, phosphorus and aluminium in zirconium minerals. P. Santini and F. Diehl (Inst. Pesquisas Tecnol., S. Paulo, Brazil). *An. Ass. Brasil. Quim.*, 1952, [1956], **11**, 167–171.—Three methods of attacking the minerals are described. One (for zirconite) is based on fusion with Na$_2$O$_2$, one (for baddeleyite) on fusion with KHSO$_4$ and making the soln. alkaline with NaOH, and the third (for baddeleyite-zirconite) on a combination of the first two methods. The titanium in the ppt. is determined colorimetrically with H$_2$O$_2$ after dissolving in HCl. Phosphorus and iron are determined by conventional methods and Al$_2$O$_3$ by difference. H. PRITCHARD

2560. The analysis of thorium-cerium binary alloys. G. W. C. Milner and G. W. Sneddon (A.E.R.E., Harwell, England). A.E.R.E. Report, C/R 1740, 1956, 15 pp.—A direct titrimetric method for the precise determination of Ce and Th in binary alloys containing up to 99% of either element is investigated on synthetic mixtures, and the following procedure is recommended. The alloys are attacked with HCl and any residue is fused with KHSO$_4$. The soln. is evaporated to fuming with HClO$_4$, then cooled and diluted to standard vol. with water. Cerium is determined on an aliquot by oxidation with S$_2$O$_8^{2-}$ and, after removal of excess of the oxidising agent, the Ce^{4+} are titrated with standard ferrous ammonium sulphate, with ferroin as indicator. Thorium is determined on a second aliquot by addition of a small known excess of EDTA and back-titration with standard Th(ClO$_4$)$_4$ at pH 2·2; the end-point is detected photometrically with Eriochrome cyanine as indicator. Typical analytical results are presented. Iron interferes, but allowance may be made for small quantities, since Fe^{3+} are titrated quantitatively under the conditions used for Th^{4+}.   D. A. PANTONY

2561. Determination of free acid in thorium salts. V. K. Zolotukhin. *Nauk. Zap. L'vivs'k. Univ.*, 1955, **34**, 138–140; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,880.—Free acid in soln. of thorium salts cannot be determined by direct titration with alkali, because of the low pH at which basic thorium salts and Th(OH)$_4$ precipitate. The thorium ions must be complexed with KF or NaF (fourfold excess) or N K or Na oxalate (tenfold excess), and the free acid is then titrated with 0·1 N NaOH to phenol red or phenolphthalein. Basic thorium salts are detected by their reaction with the alkali fluorides or oxalates, thereby forming free alkali, which is shown by the indicators.   C. D. KOPKIN

2562. Kjeldahl digestion techniques for high-temperature materials. W. Fall (Schwarzkopf Development Corp., Yonkers, N.Y.). *Powder Metall. Bull.*, 1956, **7** (3–6), 88–89.—Digestion techniques are discussed for the carbides and borides of Ti, Ta and Zr; for chromium nitride; and for Cr-Ti and Co-Cr intermetallic compounds. The results for N determined by the solution-distillation method are compared with those obtained by a vacuum-fusion method.
M. F. C. LADD

2563. Amperometric determination of phosphoric acid as the 8-hydroxyquinoline compound of molybdophosphoric acid. O. K. Serdyukova. *Nauch. Zap. L'vovsk Politekhn. Inst.*, 1955, (29), 95–99; *Ref. Zhur., Khim.*, 1956, Abstr. No. 58,460.—The method is based on the ability of Mo to be reduced at a dropping mercury cathode in HCl soln. at $-0·8$ V vs. the S.C.E. For the determination of P, use 18 ml of 8-hydroxyquinoline soln. ($M/24$), 7·2 ml of HCl (3 N) and 20 ml of (NH$_4$)$_2$MoO$_4$ (standardised by the gravimetric hydroxyquinoline method). Dilute 1 ml of the soln. ($\equiv 0·00893$ g of Mo) to 10 ml, heat to a temp. of 55° to 65° and titrate from a microburette with the soln. containing phosphoric acid. The same soln. is standardised with a known weight of phosphate. The error of determination is $\simeq \pm 4\%$.   G. BREWER

2564. A mixed screened indicator for titration of phosphoric acid. M. R. Verma and K. C. Agrawal (Nat. Phys. Lab., New Delhi). *J. Sci. Ind. Res., India, B*, 1956, **15** (12), 701–703.—The indicator is a mixture (1:1:3) of methyl orange (0·1% aq. soln.), xylene cyanol FF (0·1% aq. soln.) and phenolphthalein (0·1% ethanolic soln.). The colour at pH values $< 4·15$ is pink, between 4·50 and 8·85 light grey to yellowish green, and $> 9·05$ pink-violet; at transition points it passes through a greyish colour. The first and second H$^+$ of H$_3$PO$_4$ can be neutralised by titration against alkali, with this indicator. Any other free mineral acid present at the same time can also be estimated in a single titration.   C. A. SLATER

2565. Precipitation of zinc phosphates from solutions of sodium ortho-, pyro- and tri-phosphate. O. T. Quimby and H. W. McCune (Miami Valley Lab., Procter and Gamble Co., Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 248–253.—The addition of Zn^{2+} to soln. containing ortho-, pyro- or tri-phosphate gives 99 to 100% recovery of P at pH 5·0, but for ternary mixtures the recovery of P is only from 93 to 99%. When the pyrophosphate is separated from the triphosphate by pptn. with Zn^{2+} at pH 3·8 (Bell method), contamination of the ppt. with triphosphate occurs.
J. H. WATON

2566. Use of p-nitrophenylazoresorcinol as confirmatory test for arsenic. J. P. Mehlig and T. P. Marsh (Oregon State Coll., Corvallis, U.S.A.).

Chemist Analyst, 1957, **46** (1), 3–4.—The ppt. of magnesium ammonium arsenate, obtained after separation of As from Sb and Sn in qual. analysis, is washed with methanol, dissolved in a min. vol. of dil. HCl, one drop of a 0·5% (w/v) soln. of *p*-nitrophenylazoresorcinol in 1% NaOH is added, and the mixture is made alkaline with 6 *N* NaOH. A sky-blue lake indicates the presence of As. The limit of detection is 0·001 mg. Few anions interfere, and the test is valid in the presence of Sb, Sn^{2+} or Sn^{4+}. (*Cf. Brit. Abstr. AI*, 1940, 174.)

W. J. BAKER

2567. Determination of small concentrations of arsenic. F. V. Zaĭkovskiĭ. *Trudÿ Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 211–216; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,978.—To determine As, use a 100 to 120-ml flask with a ground glass stopper, through which passes a tube of diam. 0·5 to 0·6 cm, and length 10 to 12 cm. To the As^{III} soln. add KBr (1 g), hydrazine (0·5 g) and conc. HCl (40 ml). After mixing, close the flask with the tube, which contains a layer of wadding mixed with 0·6 to 1·0 g of KI, covered with a layer of wadding containing 0·3 to 0·4 g of KI, which is again covered with a layer of wadding. Place the flask in a beaker containing 15% $CaCl_2$ soln. (half full) and, with slow warming, raise the temp. to 110° over 15 to 20 min. Cool to between 50° and 60°, add to the flask HCl (20 ml) and KBr (0·5 g), mix and heat at 110° for 20 min. According to the concn. of As, there is formed on the sides of the tube an orange-yellow ring of AsI_3 and a dull black ring of As, of varying size. For the colorimetric determination of As, wash the AsI_3 out of the tube with hot water through a funnel containing wadding into a flask. Neutralise the soln. with a slight excess of $NaHCO_3$, add 1 or 2 ml of a saturated aq. soln. of I, and after shaking reduce the soln. with 1% ascorbic acid soln. Determine the As colorimetrically as molybdoarsenate. The error is $\not> 5\%$. C. D. KOPKIN

2568. Colorimetric determination of arsenic in sulphur. B. S. Aranovich. Report of the Symposium: *Iskusstv. Volokno.*, Issue 10, M., 1955, 85–90; *Ref. Zhur., Khim.*, 1956, Abstr. No. 65,288.—The method consists in extracting As from the sulphur with dil. aq. NH_3, oxidation to AsO_4^{3-}, and the determination of As^{5+} as molybdenum blue. Treat the finely ground sample (1 to 2 g) with 0·5% aq. NH_3 at 70° to 80° for 20 min., and filter. Treat the residue twice more with aq. NH_3, and wash with hot water. To the combined filtrates and wash liquors add Na_2CO_3 (0·5 g) and a 30% soln. of H_2O_2. Boil for 10 min., cool, add 2 ml of H_2O_2, boil for 20 min. to ensure complete decomposition of H_2O_2, and acidify with 40 or 50% H_2SO_4 until no more CO_2 is evolved. Make the soln. up to 100 ml. To 5, 10 or 25 ml of the soln. add 0·5 ml of the molybdenum reagent [10% $(NH_4)_2MoO_4$ soln. diluted with an equal vol. of conc. H_2SO_4], add a few drops of H_2SO_4 (total acidity 0·05 to 0·1 *N*), heat the soln. to boiling-point, add a piece of zinc, keep at 100° for 30 min., cool, dilute to 100 ml, and measure the extinction. Standards used were (*i*) 0·1817 g of KH_2PO_4 or 0·2325 g of K_2HPO_4 dissolved in 100 ml of 10% H_2SO_4; 5 ml of the soln. is diluted to 100 ml. To 10 ml of the resulting soln. (containing PO_4^{3-} equiv. to 0·5 mg of As) add 0·5 ml of the molybdenum reagent, 30 to 40 ml of H_2O, and a piece of zinc. Warm for 30 min., make up to 100 ml, and use as a standard. (*ii*) 0·1 g of As_2S_3 is dissolved in 0·5% aq. NH_3, Na_2CO_3 (2 g) is

added, the mixture is oxidised with 30% H_2O_2, acidified with dil. H_2SO_4, and made up to 100 ml; 10 ml of the soln. is diluted to 100 ml.

C. D. KOPKIN

2569. Separation and determination of micro quantities of arsenic and phosphorus. M. Bruno and U. Belluco (Nuclear Chem. Centre, Padua). *Ric. Sci.*, 1956, **26** (11), 3337–3341.—The microseparation and determination of components of mixtures of arsenates (or arsenites) and phosphates, alone or in the presence of other substances, is developed, with excellent results, by using chromatographic separation on a basic resin (Amberlite IRA-400) and successive colorimetric determinations. Analytical results on mixtures of arsenates (or arsenites), phosphates, and benzenesulphonates are reported. C. A. FINCH

2570. The micro-determination of arsenate in the presence of arsenite. M. Daniels (King's Coll., Univ. of Durham, Newcastle upon Tyne, England). *Analyst*, 1957, **82**, 133–135.—The sample (10 ml) is shaken with 5 ml of 2 *N* H_2SO_4, 5 ml of 5% ammonium molybdate soln. and 20 ml of *iso*butyl alcohol for 3 min., the aq. layer is discarded and the organic layer is washed twice with *N* H_2SO_4. The soln. is reduced by shaking with 30 ml of freshly diluted 0·4% $SnCl_2$ soln. in *N* H_2SO_4, the acid layer is discarded and the blue organic layer is adjusted to 25 ml with ethanol. The colour is measured in a Spekker absorptiometer with a red filter, or spectrophotometrically at 740 mμ ($\epsilon = 17,700$ litres per mole per cm). The lower limit of determination is 5×10^{-6} *M*. Tervalent As does not interfere at concn. up to 0·1 *M* and H_2O_2 only at concn. $> 10^{-3}$ *M*. Anions forming extractable *iso*poly acids with MoO_3 (*e.g.*, PO_4^{3-}, silicate and germanate) interfere and must be removed (DeSesa *et al.*, *Anal. Abstr.*, 1954, **1**, 2943). A. O. JONES

2571. Volumetric determination of antimony in antimony-lead alloys. E. G. Brown, I. P. Forshaw and T. J. Hayes (Res. Dept., British Enka, Ltd., Aintree). *Metallurgia, Manchr*, 1957, **55**, 45–47.—The alloy is dissolved in acetic acid - H_2O_2, Sb^{5+} are reduced to Sb^{3+} with aq. SO_2 soln. ($\simeq 10\%$, v/v) and, after boiling off SO_2, the soln. is titrated with 0·1 *N* $KBrO_3$, with methyl red indicator.

S.C.I. ABSTR.

2572. New colorimetric reactions for the determination of antimony. A. I. Kokorin and N. A. Polotebnova. *Trudÿ Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 205–210; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,980.—In the reduction of molybdovanadosilicic and molybdovanadogermanic acids with Sb^{3+}, blue soln. are formed. To determine Sb in type metal, dissolve the sample (0·3 to 0·5 g) in conc. H_2SO_4 (20 ml). Cool and make up to 50 ml. To reduce Sb, add to the soln. containing 100 mg of Sb in 20 ml of conc. H_2SO_4 a saturated soln. of SO_3 (1 or 2 ml) and boil to remove excess of SO_2. Cool, and add 10 ml of conc. HCl or an equivalent amount of H_2SO_4, to prevent hydrolysis. Dilute to 100 ml. Centrifuge a few ml of the soln. with the $PbSO_4$ ppt. and to 1 ml of the clear liquor add 2 ml of water and 0·2 ml of a 5% soln. of the trihetero acid. Mix, dilute to 10 ml and measure the extinction. The determination takes 1·5 hr. The presence of As does not cause interference. With molybdovanadogermanic acid the error does not exceed 0·08%.

C. D. KOPKIN

2573. Research on the polarographic characteristics of antimony and arsenic in relation to the composition of the solution and to temperature. L. D. Dolaberidze, D. K. Kamkamidze and V. K. Bugianishvili. *Sb. Nauch.-Tekh. Inform. M-vo Geol. i Okhranȳ Nedr.*, 1955, (1), 128–129; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,837.—In a basal soln. of 3 to 6 N NaOH, containing mannitol (**I**), As^{3+} and Sb^{3+} give clearly defined anodic waves. In 5 N NaOH containing 60 g per litre of **I**, $E_{\frac{1}{2}}$ for As^{3+} = 0·29 V and $E_{\frac{1}{2}}$ for Sb^{3+} = 0·48 V (vs. the S.C.E.). The height of the waves is proportional to the concn. of As^{3+} and Sb^{3+}. The temp. coeff. in the range 20° to 40° is —1·9% for As^{3+} and — 1·4% for Sb^{3+}. In these soln. no interference is caused by Cd, Pb, Zn, Bi, Mo, V, W, Cr, Al, Ca, Ba, K, Na, Fe^{3+}, Sn^{4+}, As^{5+}, Sb^{5+}, SO$_4$$^{2-}$, SO$_3$$^{2-}$, CO$_3$$^{2-}$, PO$_4$$^{3-}$ and F$^-$. In the determination of As, Co^{2+} and Mn^{2+} interfere; in the determination of Sb, Cu^{2+} and Mn^{2+} interfere. Mercury ions must be absent, since they oxidise As^{3+} and Sb^{3+}. Large quantities of Fe^{2+} interfere. To determine As in ores containing up to 5% of As and 3% of Sb and not containing Hg, decompose the ore with HNO$_3$ and H$_2$SO$_4$, remove the insol. residue and precipitate As and Fe in the filtrate with aq. NH$_3$. Dissolve the ppt. in H$_2$SO$_4$, reduce As^{5+} with hydrazine sulphate and determine the As^{3+} in a basal soln. of NaOH containing **I**, in the presence of thymolphthalein and Na$_2$SO$_3$, with the method of addition.

C. D. KOPKIN

2574. Spectrographic determination of molybdenum, beryllium, iron, chromium and nickel in bismuth and bismuth - uranium alloys. M. J. Owers and M. S. W. Webb [U.K. A.E.A. (Research Group), Woolwich, England]. *A.E.R.E. Report C/R 2115*, 1957, 15 pp.—The alloy is dissolved in HNO$_3$, the soln. is evaporated to dryness and the residue ignited at 600° to the oxides. The ground sample (as oxide) (450 mg) is ground with Bi$_2$O$_3$ containing 0·02% of V and 5% of Co as oxides (50 mg) as internal standard. The charge (70 mg) is contained in a specially designed annular graphite cup and an arc is struck to a graphite counter electrode. Spectrographic conditions are described. Concn. are derived microphotometrically with a sensitivity of 1 p.p.m. over the range 1 to 200 p.p.m., and with a variation of 6 to 12% at the 50 p.p.m. level.

D. A. PANTONY

2575. Determination of vanadium in titanium tetrachloride and titanium alloys. W. H. Owens, C. L. Norton and J. A. Curtis (Cramet, Inc., Chattanooga, Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 243–245.—Trace amounts of V in the presence of a large excess of Ti are estimated spectrophotometrically by means of the intense yellow coloration produced when a H$_2$SO$_4$ soln. of the sample is evaporated with HNO$_3$. The procedure is adapted to the analysis of Ti - Al - V alloys by adding pure TiCl$_4$ so as to keep the Ti to V ratio at $\simeq$ 200:1. Only Cr gives any serious interference.

J. H. WATON

2576. Determination of vanadium in minerals and mixtures. O. E. de Oliveira (Mineral Products Lab., Min. of Agric., Rio de Janeiro, Brasil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 193–198.— Treat the sample (400 mg) with 15 ml of conc. HNO$_3$. Evaporate to dryness, add H$_2$SO$_4$ (1:1), and heat until white fumes are given off. Cool and dilute the residue with water to 500 ml. Heat until all the V is in solution. Filter off and wash the residue (consisting principally of silica and some lead) with 1% H$_2$SO$_4$. Almost neutralise the filtrate with aq. NH$_3$ and pass H$_2$S for 10 min. Filter and wash the ppt. Make up the vol. of the filtrate to 500 ml, add 50 ml of H$_2$SO$_4$ (1:1) and 10 ml of H$_3$PO$_4$ (85%). Warm to 80° and add 0·1 N KMnO$_4$ to a permanent rose colour. Add 0·03 N Mohr's salt to decolorise, and then a measured vol. of the same salt in excess. Determine the excess by titration with 0·03 N K$_2$Cr$_2$O$_7$. H. PRITCHARD

2577. Separation of protactinium and zirconium by an anion-exchange column. A. G. Maddock and W. H. Pugh (Cambridge Univ., England). *J. Inorg. Nuclear Chem.*, 1956, **2** (2), 114–117.—Zirconium and Pa on Amberlite IRA-400 are separated by stripping 95% of the Zr containing only 0·1% of Pa with six column-vol. of 6 to 7 M HCl, and then recovering 95% of the Pa by elution with ten column-vol. of 3 M HCl or weaker acid.

CHEM. ABSTR.

2578. Determination of sulphide sulphur in the oxide layer of a cathode. V. N. Goncharova. *Trudȳ Nauch.-Issled. Inst. Min. Radiotekh. Prom.*, SSSR, 1955, [6 (26)], 40–46; *Ref. Zhur., Khim.*, 1956, Abstr. No. 71,999.—The method for the determination of H$_2$S by the formation of thionine is modified to increase the accuracy and reduce the time of the analysis. To determine sulphide S, place the cathode in a vessel, one tube of which is joined to a nitrogen cylinder, a second to two test-tubes placed in series and containing 7 or 8 ml of 0·01 N NaOH, and the third to a burette containing 25% acetic acid, which is added dropwise to the vessel in sufficient quantity to moisten the cathode. The H$_2$S which is evolved is absorbed in the NaOH soln. After clearing the H$_2$S from the vessel by passing N for 10 min., wash the soln. from the tubes into a flask, add five drops each of dil. HCl (1:4) and the reagent (10 ml of a 2·5% soln. of p-phenylene-diamine hydrochloride, 15 ml of 6 N H$_2$SO$_4$ and 25 ml of water). After 20 min. add five drops of a 5% soln. of FeCl$_3$, mix and warm for 30 sec. on the water bath at 80° to 90°. Cool, dilute to 25 ml, and measure the extinction in a 50-ml cell at 570 mμ. Determine the amount of H$_2$S from a calibration curve. The sensitivity of the method is 0·02 μg of H$_2$S per ml. The relative error is $\pm$ 10%.

C. D. KOPKIN

2579. Photometric estimation of sulphide in black liquor. R. Domanský (Bratislava, Czechoslovakia). *Chem. Tech., Berlin*, 1956, **8** (12), 731–732.—The sample (100 ml) is diluted with an equal vol. of water and titrated with either 0·1 N ammoniacal (2·5% aq. NH$_3$) AgNO$_3$ or 0·1 N aq. HgCl$_2$ (each gives equally accurate results), a platinum indicator electrode and a S.C.E. being used. A little ethanol should be added to the sample to avoid coagulation of org. compounds on the electrodes, etc. The method is much more rapid and more accurate than the TAPPI method; it gives results $\simeq$ 6% higher as it avoids the H$_2$S losses of the TAPPI method. Its accuracy is not affected by the presence of OH$^-$, CO$_3$$^{2-}$, SO$_3$$^{2-}$, S$_2O_3$$^{2-}$, SO$_4$$^{2-}$ or Cl$^-$.

H. L. WHITEHEAD

2580. Colorimetric determination of sulphate with barium chloranilate. R. J. Bertolacini and J. E. Barney, II [Res. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1957, **29** (2), 281–283.—Sulphate is determined spectrophotometrically as the acid chloranilate ion released

when excess of Ba chloranilate is added to a 50% aq. ethanol soln. at pH 4. The $BaSO_4$ and excess of Ba chloranilate are removed by centrifuging and the extinction of the soln. is measured at 530 mμ against a blank. Cations must be removed previously by ion exchange, and anions may interfere if they form insol. barium compounds. Under the conditions of the analysis, 100 p.p.m. of Cl^-, NO_3^-, HCO_3^-, PO_4^{3-} and $C_2O_4^{2-}$ give no interference, and as little as 2 p.p.m. of SO_4^{2-} can be determined. The precision of the method is $\simeq 1\%$. The procedure can be extended to the determination of S whenever it can be converted into SO_4^{2-}, e.g., S in fuel oils. J. H. WATON

2581. **The volumetric determination of sulphate using a high-frequency conductimetric method.** G. R. Jamieson (Technical College, Paisley, Scotland). *J. Appl. Chem.*, 1957, **7** (2), 81–86.—As this apparatus has no electrodes in the titration cell, errors due to deposition of the ppt. on the metal electrodes are obviated. Of the precipitants tested, barium acetate (**I**) gave accurate results in the presence of Cl^-, but NO_3^- interfered. Octa-ammino-μ-amino-μ-nitrodicobaltic tetranitrate (**II**) and hexa-amminocobaltic bromide (**III**) both gave good results and were not affected by the presence of NO_3^- or Cl^-. The Na_2SO_4 was dissolved in ethanol - water for **I** and **III** and in acetone - water for **II**. All titrations were made in neutral soln. F. J. M.

2582. **Complexometric determination of sulphate ion using diethylenetriaminepenta-acetic acid.** E. Wänninen (Dept. of Inorg. and Anal. Chem., Åbo Akad., Turku, Finland). *Suomen Kem., B*, 1956, **29**, 184–188.—Barium chloride is added in excess to the sulphate soln. and the excess titrated at pH 10 with the trisodium salt of diethylenetriaminepenta-acetic acid (DTPA) in the presence of magnesium - DTPA and Eriochrome black T. This titrimetric method is superior to that with EDTA because of the greater stability of the barium - DTPA complex. For sulphate in the range 0·1 to 0·3 millimole the mean error was about 0·25%. M. F. C. LADD

2583. **Complexometric estimation of sulphate with phthaleincomplexone.** B. Philipp and H. Hoyme (Dtsch. Akad. Wissensch., Inst. Faserstoff-Forsch., Teltow-Seehof, Berlin). *Faserforsch. u. Textiltech.*, 1956, **7** (11), 525–527.—A description is given of the estimation of sulphate (free and combined H_2SO_4) in aq. solutions (especially viscose spinning baths) by pptn. as $BaSO_4$ and titrating the Ba with EDTA (disodium salt) (**I**), either directly, with phthaleincomplexone as indicator, or by a replacement titration in which Ba is replaced by Zn or Mg before titration with **I**, with Eriochrome black T as indicator. Tests show the methods to have at least the accuracy of gravimetric methods and to take less than one-tenth the time. Optimum conditions for accuracy (especially sulphate contents) are worked out and the effect on the accuracy of the presence of NaCl, NaBr, Na_2SO_3, Na_2S and Fe has been determined. H. L. WHITEHEAD

2584. **The precipitation of quadri- and sexa-valent selenium with sulphur dioxide.** H. Bode and H.-D. Stemmer (Anorg.-chem. Inst., Tech. Hochschule, Hannover, Germany). *Z. anal. Chem.*, 1957, **155** (2), 96–105.—A rapid and complete pptn. of Se^{4+} is carried out by using a 0·5 to 1 N HCl soln., a closed vessel to prevent loss of SO_2, and a temp. of

about 100°. To the sample in a stout-walled 120-ml rubber-stoppered flask add aq. SO_2 soln. (satd. at 20°) (5 ml per 100 mg of Se) and HCl to make the soln. $\not< 0·5$ N. Place the flask on a cold-water bath, heat to boiling-point and maintain this temp. for 60 min. for 0·5 N HCl soln. or 30 min. for 1 N. Cool the flask to room temp., filter the contents and wash the ppt. with H_2O containing SO_2 and HCl at the same concn. as used for the pptn., then with water, ethanol and ether. Dry for 30 min. at 130° and weigh. For soln. containing both Se^{IV} and Se^{VI}, Se^{4+} are pptd. first as described above, the filtrate (containing the Se^{6+}) is made 4 to 5 N to HCl, and the resulting Se^{4+} are pptd. similarly. G. BURGER

2585. **Separation and photometric determination of small amounts of selenium and tellurium by means of thiourea.** A. Jílek, J. Vřešťál and J. Havíř (Military Tech. Acad., Brno, Czechoslovakia). *Chem. Zvesti*, 1956, **10** (2), 110–114.—Small amounts (0·2 to 2 mg) of Se and Te can be determined in mixtures by the use of thiourea. Selenium is pptd. with a saturated soln. of thiourea in 0·8 N $HClO_4$ and separated by centrifuging. The filtrate, containing a yellow tellurite complex, is heated for 5 min. on a water bath, and the colour is measured directly or, preferably, after reduction of the soln. with $SnCl_2$. The Se-containing ppt. is dissolved in HCl - Br, reduced with hydroxylamine in the presence of a protective colloid, and determined photometrically. J. PELIKÁN

2586. **Automatic spectrophotometric titrations: determination of chromium, titanium and vanadium in titanium materials with electrolytically generated titrant.** C. B. Roberts (Univ. Illinois, Urbana, U.S.A.). *Dissert. Abstr.*, 1956, **16** (10), 1798–1799.—An automatic derivative spectrophotometric titrator is described that is applicable to soln. where there is a sharp change of absorbance at the end-point even though the absolute absorbance is unknown. The results for some common acid - base and redox titrations show 0·1% precision. In the determination of Fe in titanium sponge, alloys and ores, Fe^{3+} are automatically titrated with electrolytically generated Ti^{2+}. The mean absolute error is about 0·003% of Fe over a range of 0·01 to 20%. In the determination of Ti, aliquot samples are passed through a cadmium reductor into standard $FeCl_3$ soln. containing sufficient Ti^{4+} for electrolysis purposes. The excess of Fe^{3+} is then titrated as above. Chromium and Fe in titanium can be determined with one titration after oxidation to Cr^{VI} and Fe^{III}; Cr is first reduced to Cr^{III} by electrolytically generated Ti^{2+}, with diphenylamine sulphate as indicator. After adding leuco methylene blue, the titration is continued and the Fe^{III} is reduced to Fe^{II}. Vanadium in $TiCl_4$ is determined by hydrolysing the latter and using the automatically recorded absorbance vs. milli-equiv. curve. N. E.

2587. **Analytical solvent extraction of molybdenum using acetylacetone.** J. P. McKaveney and H. Freiser (Univ. of Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 290–292.—Acetylacetone - $CHCl_3$ (1:1) will selectively extract Mo from 6 N H_2SO_4 soln. By this means Mo in ferrous material can be determined in the presence of Cu, Cr and W. The analysis is completed by the colorimetric determination of the Mo - thiocyanate complex in the presence of $SnCl_2$. J. H. WATON

2588. The micro-detection and colorimetric micro-determination of molybdenum(VI) with morin. G. Almássy and M. Vigvári (Phys. Res. Inst., Hungarian Acad. Sci., Debrecen, Hungary). *Magyar Kém. Foly.*, 1956, **62** (10), 332–335.—Morin (**I**) and Mo^{VI} form a brownish complex which is soluble in *n*-butanol (**II**). The interference of other ions is eliminated by means of EDTA (disodium salt) (**III**) or NaF. *Procedure*—For the qual. test, add a 2·5% soln. of **III** (3 ml) and satd. NaF soln. (0·5 ml) to the unknown soln. (5 ml, $\simeq$ 0·1 to 0·5 N with respect to HCl) followed by **II** (2 ml) and a 0·33% soln. of **I** in **II** (0·5 ml). Shake for 10 to 15 sec. If Mo^{VI} is present, the layer of **II** becomes orange coloured. The sensitivity is 0·05 μg of Mo^{VI} in 5 ml. Ions that do not interfere are discussed. For the quant. determination, extract thrice a 0·1 to 0·5 N HCl soln. (20 ml) containing Mo^{VI} (5 to 30 μg) with mixtures of **II** (3 to 5 ml) and a 0·33% soln. of **I** in **II** (0·5 ml), and dilute the combined extracts with **II** to 15 ml. The soln. is estimated in a Pulfrich photometer, with an S43 filter (430 mμ) and a 3-cm cell. When other ions are present, carry out the extraction in the presence of **III**. The lower limit of determination is 1 μg of Mo^{VI} in 20 ml of original soln.

A. G. PETO

2589. Studies of gallic acid complexes with metals and their analytical applications. II. Spectrophotometric study of molybdenum complexes. M. S. Varde and V. T. Athavale (Atomic Energy Estab., Bombay). *Proc. Indian Acad. Sci., A.*, 1956, **44** (4), 228–240.—Spectrophotometric study of the Mo - gallic acid system shows the formation of a yellow complex of the empirical formula $MoC_7H_6O_5$, with an absorption max. at 305 mμ. The complex dissociates appreciably in solution and gives a value of $0·6 \times 10^{-4} \pm 0·1 \times 10^{-4}$ for the dissociation constant. Beer's law holds for concn. up to 1 mg of Mo per 100 ml, and quant. estimations can be made after isolation of Mo from interfering elements such as Fe, Ti, V and W. Addition of complexing agents, *e.g.*, tartaric or oxalic acid, or EDTA, either diminishes or destroys the colour due to Mo.

I. JONES

2590. Anion-exchange separation of molybdenum and technetium and of tungsten and rhenium. E. H. Huffman, R. L. Oswalt and L. A. Williams (Univ. of Calif., Berkeley, U.S.A.). *J. Inorg. Nuclear Chem.*, 1956, **3** (1), 49–53.—Dowex-1 (Cl⁻ form) is used for the separations. Molybdenum is separated from Tc by elution with N HCl, and the Tc is eluted with 4 N HNO₃. Tungsten is separated from Re by elution with 1·5 N HCl, and the Re is eluted with 4 N HNO₃. The variations of K_D with HCl concn. for Tc and Re with Dowex-1 (Cl⁻ form), and with HNO₃ concn. for Mo, Tc, W and Re with Dowex-1 (NO₃⁻ form) are given.

G. J. HUNTER

2591. The determination of molybdenum and tungsten. X. Colorimetric determination of molybdenum with potassium ethylxanthate. Shu-Chuan Liang and Pao-Yun Hsu (Inst. of Chemistry, Academia Sinica, China). *Acta Chim. Sinica*, 1956, **22**, 171–176.—Certain aspects of the ethylxanthate reaction for Mo were examined. Max. stability of the molybdenum xanthate complex (**I**) in aq. soln. was found in 0·02 to 0·08 N HCl (pH 1·11 to 1·56), with chlorobenzene and CCl_4 as extractant. The time of shaking should be $\not>$ 1 min. The colour of **I** was stable for at least three days in light petroleum

and toluene, for 14 min. in benzene, for 10 min. in CHCl₃, for 7 min. in chlorobenzene and 6 min. in CCl_4. Diethyl ether, *iso*amyl alcohol, amyl acetate and *iso*butyl methyl ketone were found to be unsuitable as extractants. The efficiency for the extraction of **I**, judged by the optical density, was chlorobenzene > benzene = toluene > CHCl₃ > CCl_4 > light petroleum. Beer's law was obeyed for 0 to 0·4 mg of Mo in chlorobenzene, 0 to 0·3 mg in benzene and toluene, and 0 to 0·2 mg in CHCl₃ and CCl_4. Toluene is recommended as the most suitable extractant.

S. H. YUEN

2592. Determination of molybdenum and tungsten. IX. Estimation of tungsten as barium tungstate. Shu-Chuan Liang and Pao-Yun Hsu (Inst. Org. Chem., Acad. Sinica, China). *Acta Chim. Sinica*, 1956, **22**, 93–102.—Factors affecting the gravimetric determination of tungstate as barium tungstate (**I**) were critically examined and optimum conditions are recommended. **I** was best pptd. from a boiling soln. of pH 7·2 to 8·0 with excess of $BaCl_2$. At this pH range, pptn. of carbonate (from CO_2 in air and H_2O) and chloride (from $BaCl_2$) was not appreciable ($< 0·4\%$). The concn. of $BaCl_2$ after pptn. should be maintained within 0·8 to 2 mM for acceptable results. Ignition of **I** was preferably carried out at 500° to 900°. Drying at 105° or 150° gave results that were 0·2 to 0·3% high presumably owing to incomplete removal of H_2O. Sodium and ammonium acetate ($\not> 4$ g) did not interfere with the test, but 0·5 g of KCl caused a negative error. This method may be used to estimate as little as 6 mg of WO_3.

S. H. YUEN

2593. The reaction of uranyl ion with xanthates and diethyldithiocarbamate. R. A. Zingaro (A. and M. Coll., Coll. Station, Texas, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 3568–3570.—It has been found that UO_2^{2+} will, in the presence of K⁺, form ppt. with some xanthates and with diethyldithiocarbamate corresponding to KUO_2X_2, where X is a xanthate or diethyldithiocarbamate radical. Spectrophotometric data indicate a double-salt structure for the diethyldithiocarbamate complex of the type $UO_2X_2.K_2UO_2X_4$.

C. A. SLATER

2594. Identification of uranium. L. F. de Carvalho (Mineral Products Lab., Min. of Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 127–129.—When exposed to light, uranyl salts have the property of decomposing oxalic acid or oxalates to give formic acid or formates. This property combined with that of the formate ion of reducing mercuric salts to mercurous salts (*cf.* Feigl and Goldstein, *Anal. Abstr.*, 1957, **4**, 2649) is used for the identification of U. Place a drop of the test soln. and a drop of saturated Na oxalate soln. on a tile. Evaporate on a water bath to dryness. Expose the crystalline residue to u.v. light for 30 min. Add a drop of buffer soln. (1 ml of glacial acetic acid and 1 g of Na acetate, made up to 100 ml), a drop of $HgCl_2$ soln. (1%) and evaporate to dryness on a water bath. Cool and add a drop of aq. NH₃ and the presence of U is revealed by the appearance of a black spot, which contrasts clearly with the crystalline mass. This method is sensitive to 2·5 μg of U per drop. Iron, > 100 μg per drop, interferes, but not the rare earths.

H. PRITCHARD

2595. Coulometric determination of uranium(VI) at controlled potential. G. L. Booman, W. B. Holbrook and J. E. Rein (Atomic Energy Div.,

Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 219–221.—A rapid high-precision method for determining U in the presence of large amounts of HNO_3 involves the reduction of U^{VI} to U^{IV} at a controlled potential. For samples containing < 2 mg of U, a M K citrate - $0.1 M$ $Al_2(SO_4)_3$ electrolyte (pH 4.5) is used, and for samples containing > 2 mg of U the electrolyte is M H_2SO_4. The reductions are carried out at -0.60 V (after a pre-reduction at -0.20 V) and -0.25 V, respectively, all voltages measured *vs.* a silver - silver chloride - saturated KCl electrode. The determination is possible in the presence of excess of Hg^{II}, and smaller amounts of Cu^{II} and Fe^{III}. The standard deviation is $< 0.1\%$ for amounts of U in the range 75 to 0.75 mg.

J. H. WATON

2596. The absorptiometric determination of micro-gram quantities of uranium with the thoronol complex of quadrivalent uranium. J. K. Foreman, C. J. Riley and T. D. Smith (U.K. Atomic Energy Authority, Windscale Works, Sellafield, Calder-bridge, England). *Analyst*, 1957, **82**, 89–95.—In dil. acid, U^{IV} forms a red complex with thoronol [the red sodium salt of 1-(o-arsonophenylazo)-2-naphthol-3 : 6-disulphonic acid] which is stable in aq. acetone. The sample in dil. HCl or HNO_3 soln. is treated with aq. cupferron soln. and extracted with $CHCl_3$. The separated aq. layer is treated with satd. EDTA soln., made alkaline, and buffered to pH 6 with a Na acetate - acetic acid buffer; aq. Na diethyldithiocarbamate soln. and $Ca(NO_3)_2$ soln. are added, the pH is re-adjusted and the liquid is extracted with $CHCl_3$. The $CHCl_3$ extract is then extracted with ammonium carbonate soln., the extract is evaporated to dryness and the residue is ignited, dissolved in HCl and shaken with freshly cleaned lead shot. The soln. (2 ml) is mixed with 20 ml of acetone and 1 ml of 0.5% thoronol soln., and the vol. is adjusted to 25 ml with water. The extinction is measured in a Spekker absorptio-meter with Ilford No. 605 filters, against a blank prepared by the same procedure with omission of the sample. A. O. JONES

2597. Analysis of uranium and thorium minerals by α-spectrum. U. Facchini, M. Forte, A. Malvicini and T. Rossini (Lab. CISE, Milan, Italy). *Nucle-onics*, 1956, **14** (9), 126–131.—Spectral analysis of the α-particles emitted by the mineral is made by using a grid ionisation chamber. Sources are prepared by spreading the finely ground mineral over a disc, 14 cm in diameter. Sodium silicate and gelatin (20% w/w) have been used as bonding agents. Total source weights of 3 to 20 mg are suitable. Measurement of the ^{238}U and Th-C′ lines enables the U to Th ratio to be determined when this is between 0.1 and 10. The content of Ra can be assessed from measurement of the Ra-A and Ra-C′ lines. The sensitivity is such that 100 μg of U gives $\simeq 300$ counts per min. G. J. HUNTER

2598. Acetylacetone as analytical extraction re-agent. Increase in selectivity with (ethylenedi-nitrilo)tetra-acetic acid and analytical separation of uranium from bismuth. A. Krishen and H. Freiser (Univ. of Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 288–290.—The presence of EDTA (disodium salt) increases the specificity of acetyl-acetone as an extraction reagent. In this way U can be separated from up to 5000 times as much Bi, and is then determined polarographically with an error (relative) of $\pm 1\%$. J. H. WATON

2599. Chromatographic separation of fluoride and phosphate. I. Zipkin, W. D. Armstrong and L. Singer (U.S. Dept. of Health, Educ. and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 310–311.—Fluoride is quant. separated from excess of PO_4^{3-} by elution with $0.5 N$ NaOH from a Dowex 1-X10 (OH^- form) ion-exchange column; as little as 25 μg of F^- can be recovered from a 500-fold excess of P. The same ions are also separated by paper partition chromatography on Whatman No. 3MM paper strips, with an aq. NH_3 $(2 N)$ - abs. methanol solvent (30 : 70 v/v). The R_F values for F^- and PO_4^{3-}, whether alone or together, are 0.65 and 0.34, respectively. Both ions are identified by spraying with zirconium - alizarin reagent.

J. H. WATON

2600. Mercurimetric determination of chlorides and bromides. N. A. Novikovskaya and E. S. Przheval'skii. *Tr. Vses. Nauch. Inst. Khim. Reaktivov.*, 1956, (21), 33–37; *Ref. Zhur., Khim.*, 1956, Abstr. No. 58,475.—The method is based on the reaction $Hg_2(NO_3)_2 + 2X^- \rightarrow Hg_2X_2 + 2NO_3^-$, where X^- is Cl^- or Br^-. The titration is carried out with diphenylcarbazide as indicator; this forms with excess of $Hg_2(NO_3)_2$ a ppt. with an intense blue colour. G. BREWER

2601. Spectrophotometric determination of chlo-ride, bromide and iodide. F. W. Chapman, jun., and R. M. Sherwood (Atlantic Refining Co., Philadel-phia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 172–176.—Microgram quant. of Cl^-, Br^- and I^- are determined spectrophotometrically after reaction with aq. $PdSO_4$ soln. Measurements for Cl^- and Br^- are made at 230 mμ, and for I^- at 390 mμ. A separation can be achieved by using selective oxidation of the halides. The I^- are destroyed with no loss of Br^- and Cl^- by warming with MnO_2, in slightly acid soln.; I^- and Br^- are destroyed with no loss of Cl^- by heating with PbO_2 in slightly acid soln. This method can be applied to samples of petroleum naphtha which are treated with diphenyl sodium to convert organic into ionic halides, and cracking catalysts which are first fused with Na_2CO_3. Interference from the Na introduced by the fusion is overcome by passing the aq. soln. of the sample through a cation-exchange resin. The total time for the analysis of a petroleum sample is $\simeq 12$ hr.; the precision and accuracy show a coeff. of variation of $\simeq 5\%$. J. H. WATON

2602. Polarographic estimation of lead, copper and zinc in solutions of sodium chloride. H. Funk and H. Schäfer (Inst. Inorg. Chem., Martin Luther Univ., Halle-Wittenberg). *Chem. Tech., Berlin*, 1956, **8** (12), 718–725.—The micro apparatus of Heyrovský, operating at a constant temp. of 25°, with a dropping electrode (internal diam. 0.06 mm.; dropping time 3 sec.) and a calomel electrode, has been used to investigate the estimation of Cu, Pb and Zn in conc. ($\simeq 1$ to 2 M) soln. of NaCl. Of the methods tried, the following gives reliable results with all relative proportions of Cu, Pb and Zn, and is equally applicable to soln. in conc. aq. NaCl or $CaCl_2$. Copper is estimated in the presence of EDTA with an initial potential of -0.25 V and proceeding via the critical potential for the Cu step (-0.7 to -1 V) until the Pb step is reached (at -2 V). Good results for Pb are not obtained by using the Pb step, and there is no Zn step. For Pb and Zn, a fresh sample is taken and the Cu is first removed by electro-deposition of the acidified sample at constant cathode potential (-0.35 V).

For Pb, the polarogram is taken of the resulting solution (after neutralising) at -0.7 to -1.1 V. For Zn, the electro-deposition is continued at -0.7 V to remove Pb, and the polarogram of the resulting solution is taken at -1.3 to -1.8 V.

H. L. WHITEHEAD

2603. Determination of hydrobromic acid in bromine. D. Kaplan and I. Schnerb (Research Council of Israel, Jerusalem). *Bull. Res. Counc. Israel, C,* 1956, **5** (2–3), 178–180.—Bromine containing HBr is shaken with 0.25 N KBr, thereby extracting the whole of the HBr. The Br in the KBr solution is expelled by an air current and the HBr titrated with 0.01 to 0.02 N NaOH. Any HBr formed during the test by hydrolysis is determined by running a blank with HBr-free bromine.

S.C.I. ABSTR.

2604. Polarographic determination of trace quantities of iodide. S. W. Smith and J. K. Taylor (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *Anal. Chem.,* 1957, **29** (2), 301–303.—The procedure described by Rylich (*Coll. Czech. Chem. Commun.,* 1935, **7**, 288) for the polarographic estimation of I^- after oxidation to IO_3^- is adapted to the determination of trace quantities. With 1 ml of soln. the limit of the determination is $\simeq 0.03$ μg and the accuracy is within $\simeq \pm 5\%$. The presence of Cl^- and Br^- does not cause interference, but relatively large amounts of heavy metals and certain types of reducible organic matter should be removed.

J. H. WATON

2605. Manganon IREA—a new reagent for manganese. I. Some methyleneimines as reagents for cations. A. M. Lukin and E. D. Osetrova. *Tr. Vses. Nauch. Inst. Khim. Reaktivov.,* 1956, (21), 3–9; *Ref. Zhur., Khim.,* 1956, Abstr. No. 58,441.—Condensation compounds of salicylaldehyde with *o*-aminophenylarsonic acid, anthranilic acid and *o*-aminophenol were prepared and also compounds by substituting one or both benzene rings in these compounds by naphthalene. *o*-Salicylideneaminophenol (**I**) (manganon IREA) was found to give a sensitive colour with Mn^{2+} (0.25 μg).

II. The reaction between manganon IREA and manganese (II). G. G. Karanovich, A. M. Lukin, E. D. Osetrova and R. E. Chernitskaya. *Ibid.,* 1956, (21), 10–13.—The change of colour of a 0.05% ethanolic soln. of **I** at pH 9.6 to 11.6 from yellow to brown is due to oxidation by air; this is catalysed by Mn^{2+}, the acceleration being proportional to the concn. of Mn^{2+}. The oxidation can be stopped by adding formaldehyde soln., and the colour is measured.

III. The colorimetric determination of small quantities of manganese (II) with manganon IREA. G. G. Karanovich. *Ibid.,* 1956, (21), 14–17.—Details are given for the colorimetric determination of Mn^{2+} (0.25 to 8 μg) in 5 ml of soln. In proportions (Mn:M) up to 1:200 As and Cd, up to 1:100 Ag and Mo and up to 1:50 Zn, Al and Hg^{2+} do not interfere. Up to 1:100 of Cr^{3+} and Ba or up to 1:50 of Fe^{3+}, Ni^{2+} and Mg do not interfere if they are masked with Na K tartrate. Interference is caused by Pb, Co and Cu.

G. BREWER

2606. Spectrographic determination of manganese in the presence of aluminium. R. T. Buccheri (Laminação Nacional de Metais, Utinga, S. Paulo, Brazil). *An. Ass. Brasil. Quím.,* 1953, [1956], **12** (1), 5–11.—A routine method is described for the complete analysis of aluminium 3S, in particular for

the determination of Mn. A sample of the metal is cast into four cylindrical electrodes (4 cm $\times$ 5 mm). In the same way four controls containing from 0.43 to 1.45% of Mn are prepared which serve to produce a reference curve. The wavelengths selected as most suitable are 2669.16 A as internal control, and 2688.24 A for Mn. A set of samples was examined by the spectrographic and chemical methods, and it was found that the greatest difference observed was about 3.4%. The causes of error in the spectrographic method are discussed.

H. PRITCHARD

2607. Polarographic determination of trace elements in manganese metal and salt solutions. I. Simultaneous determination of traces of copper, cadmium, nickel and zinc. Y. Israel (Israel Mining and Industries Lab., Haifa). *Bull. Res. Counc. Israel, C,* 1956, **5** (2–3), 171–177.—A procedure is described for the simultaneous determination of traces of Cu, Cd, Ni and Zn in electrolytic manganese metal (99.8 to 99.95% pure) and in purified electrolytic manganese salt solutions, with an M NH$_4$Cl - M aq. NH$_3$ supporting electrolyte. The base solution also contains 5% of $(NH_4)_2SO_4$ (to eliminate interference of Pb on the Cu wave), 0.01% of gelatin as maxima suppressor and 2% of Na_2SO_3 to eliminate dissolved O. Standardised procedures for the prep. of test samples and blanks are defined, and calibration curves are given of trace elements in the 2×10^{-3} to 1 mM concn. range.

S.C.I. ABSTR.

2608. Spectrographic analysis of high-speed and stainless steels. P. A. Artamonova. *Trudy Leningr. Metal. Zavod.,* 1955, (2), 106–111; *Ref. Zhur., Khim.,* 1956, Abstr. No. 65,346.—In determining W, Cr and V in high-speed steels, samples and standards are cast as cylinders, of diam. 30 mm. The spectra are excited by the condensed spark discharge from generator IG-2, with copper electrodes, and photographed on the medium spectrograph with a two-step filter under the following conditions—spark gap 2.5 mm, discharge gap 3 mm, capacity 0.01 μF, self-induction 0.01 mH, current 1.7 amp. Diapositive plates were used, the slit width was 0.02 mm, the preliminary sparking time was 1 min. The lines used analytically were W 2397 - Fe 2396.7; Cr 2782.3 - Fe 2793.8; V 3130.3 - Fe 3083.15 A. In the analysis of stainless steels, the standards were manufactured samples of steel of arbitrary shape. The determination of Cr was carried out from the lines Cr 3147.2 - Fe 3154.5 A, with generator IG-2 under the conditions given above. The determination of Mn, Si and Ni was carried out from the lines Mn 2939.3 - Fe 2944.4; Si 2506.9 - Fe 2507.9; Ni 3414.0 - Fe 3399.3 A in the a.c. arc discharge with burning time 10 sec., current strength 4 amp. and arc gap 2 mm. Good agreement is indicated between the results of chemical and spectrographic analyses.

C. D. KOPKIN

2609. Colorimetric determination of aluminium in steel by means of stilbazo. N. A. Agrinskaya and V. I. Petrashen'. *Tr. Novocherkas. Politekh. Inst.,* 1955, **31**, 63–71; *Ref. Zhur., Khim.,* 1956, Abstr. No. 58,412.—Stilbazo [ammonium 4:4'-di-(3:4-dihydroxyphenylazo)stilbene-2:2'-disulphonate] has a maximum absorption in the u.v. range, but that of its compound with Al^{3+} is at 496 mμ. The complex is stable. The colorimetric determination must be carried out at pH 3.6 to 5.6 (acetate buffer). The soln. obeys Beer's law in the range

0·1 to 1 μg of Al per ml. In forming the complex, one atom of Al requires 1 mol. of stilbazo. The molar coefficient of extinction is 34,600. A method was worked out for the colorimetric determination of 0·01 to 0·025% of Al in steel in the presence of Cr, Mo and V, after the electrolytic separation of the Fe. The method gives accurate results, the average error being 2·6% (relative). G. BREWER

2610. Spectrographic determination of carbon in steel. L. V. Popov and R. V. Sokolova. *Uch. Zap. Kazansk. Univ.*, 1955, **115** (12), 25–39; *Ref. Zhur., Khim.*, 1956, Abstr. No. 65,305.—The optimum set of conditions is described for the discharge of a low-voltage spark in the determination of carbon. A comparison is made of the results of the use of a low-voltage and a high-voltage spark. The work was carried out on a medium spectrograph with slit width 0·02 mm. The plates were diapositive, with extra contrast. The low-voltage spark, following Abramson (*Zhur. Tekh. Fiz.*, 1949, **19**, 611; *Zavod. Lab.*, 1948, **14**, 1135), was produced with the parameters $C = 10$ μF, $C_1 = 0·01$ μF, $C_2 = 100$ cm, self-induction $= 9500$ cm, $R = 65$ ohms and $R_1 = 10,000$ ohms. The analytically used lines were C 2296·89 - Fe 2298·23 A. The upper electrode was of copper, current 4 amp., spark gap 1 mm. Sparking was for 40 sec., exposure 80 sec. The calibration curve on the co-ordinates ΔS - log C has a slope of 0·5. To obtain the high-voltage spark, the generator IG-2 was used, without self-induction, with capacity 0·02 μF, current 3 amp. The spark gap was 1 mm, exposure time 1 min., sparking time 20 sec. The low-voltage spark is most useful for concn. of 0·2 to 0·8%, and the high-voltage spark for concn. of 0·2 to 1·2%. With the high-voltage spark, the control standard method gives good accuracy. The probable error is within the limits 4 to 7%. C. D. KOPKIN

2611. Determination of carbon and sulphur in the same sample [of steel]. L. Bjerkerud. *Jernkontor. Ann.*, 1955, **139** (10), 847–852.—The gases from the combustion furnace are bubbled through a soln. of starch and KI contained in a vessel which is connected with a burette delivering standard $Na_2S_2O_3$. The iodine liberated by the SO_2 is continuously titrated throughout the combustion, the end-point being adjusted during the final stages. The SO_2-free gases are passed through a known vol. of standard NaOH soln., and the amount of CO_2 absorbed is determined by a titration method. A by-pass is provided when C only is to be determined; for this purpose an absorption tube containing dichromate soln. intervenes before the gases reach the CO_2-absorption vessel. The reproducibility of the method is satisfactory, and the results are in good agreement with those obtained in separate determinations of C and S. P. S. ARUP

2612. Improved method for the colorimetric determination of silicon in cast iron. R. Moshtev. *Dokl. Bolgar. Akad. Nauk*, 1955, **8** (2), 25–28; *Ref. Zhur., Khim.*, 1956, Abstr. No. 65,310.—Treat the sample of cast iron (0·5 to 5% of Si) by warming with H_2SO_4 (1:8) (10 ml) on a water bath heated to between 80° and 90°. Add HNO_3 (1:3·5) (5 ml), warm for another 2 or 3 min., cool and dilute to 250 ml. To 5 ml of the soln. obtained, add 0·15 N H_2SO_4 (8 ml), and 5% ammonium molybdate soln. (4 ml); mix, and after 3 or 4 min. add 8 N H_2SO_4 (12 ml) and 0·3% hydrazine hydrochloride soln. (4 ml), mix and warm for 5 min. on the water bath.

Cool, dilute to 50 ml, and measure the extinction on the Pulfrich photometer with red filter S72, in a 1- or 2-cm cell. The colour is stable for several hours. At the same time a control experiment is carried out, with a ferric soln. The calibration curve is constructed from soln. of cast iron with known content of Si. Beer's law is observed for 0·2 to 2 μg of Si per ml. With 2·5 to 4% of Si the error is ± 0·05%. C. D. KOPKIN

2613. Rapid determination of silicon in cast iron in foundry practice. J. Gremminger and L. Piatti (Lab. der Gebrüder Sulzer A.-G., Winterthur). *Chimia*, 1957, **11** (2), 48–50.—In cast iron, 80 to 90% of the Si is present as FeSi and this is convertible by strong acids into insoluble silicic acid, which can be ignited to SiO_2. The sample is first heated with $HClO_4$ to accelerate dissolution and decompose carbide and phosphide. After filtration, the silicic acid is heated in a stream of O in a muffle-furnace at 1000° to 1100°. The total time of treatment for a 200-mg sample was 10 min. Specified times are given for each stage of treatment; for evaporation and incineration, they should not be < 3 min. each, since shorter times might cause pptn. of colloidal silicic acid, and complete combustion of any graphite present might be prevented. W. J. WRIGHT

2614. Photometric determination of arsenic in technical iron by silver diethyldithiocarbamate. Z. Večeřa and B. Bieber (Výzkumný ústav materiálu a technol., výzhum slévárenský, Brno). *Slévárentství*, 1956, **4**, 366–370.—The method described is applicable to cast iron, carbon steel or pig iron. The sample is dissolved in HNO_3 - H_2O_2 (100 vol.) and fumed with H_2SO_4. Arsine evolved is passed into a solution of Ag diethyldithiocarbamate in pyridine, with the formation of an intense red colour. The Beer - Lambert law is obeyed in the range 0 to 40 μg of As per 10 ml of solution. S.C.I. ABSTR.

2615. Colorimetric determination of molybdenum in steel. F. Bermejo Martínez and A. Prieto Bouza (Fac. de Ciencias de la Univ. de Santiago). *Quim. e Ind., Bilbao*, 1956, **3** (4), 168–172.—The determination is carried out by formation of $Mo(SCN)_5$, extraction of this complex by amyl alcohol - CCl_4 and measurement of the extinction of the extract at 465 mμ. *Procedure (i)*—For steels containing up to 1% of W, a 0·1-g sample is dissolved in 5 ml of conc. HCl, 0·05 g of $KClO_3$ is added and when the reaction is complete the soln. is boiled to remove Cl. The soln. is treated in a platinum crucible with HF and conc. H_2SO_4 to remove Si, and evaporated to dryness. The residue is taken up in 5 ml of conc. HCl and diluted to 100 ml. A 10-ml aliquot is neutralised with conc. aq. NH_3, 10 ml of 6·5 N HCl is added and the soln. is diluted. If Ti is present, 5 ml of satd. NaF soln. is added, followed by sufficient EDTA (disodium salt) to complex the cations present. The soln. is boiled for 10 min., cooled, transferred to a separating funnel, diluted to 45 ml, then saturated by shaking with 3 ml of amyl alcohol - CCl_4 (1:1). Excess of solvent is separated, and the colour is developed by adding 1 ml of KSCN soln. (40%) followed by 1 ml of $SnCl_2$ soln. (40%) and extracted with 15 ml of amyl alcohol - CCl_4 (1:1). The extinction is measured, a 2-cm cell and a blue filter (465 mμ) being used. For samples containing > 0·5% of Mo the extract must be diluted before measurement of its extinction. A blank determination is carried

out on the reagents, and a calibration graph is constructed from a standard solution of Mo. *Procedure* (*ii*)—For steels containing $> 1\%$ of W, a 0·1-g sample is dissolved in 5 ml of conc. HCl, 0·4 g of Na_2HPO_4 is added and the soln. is boiled. After attack is complete, 2·5 ml of $KClO_3$ soln. (5%) is added, the soln. is boiled to remove Cl, and the determination is completed as described in procedure (*i*). The following elements do not interfere—Ni, Cr, Co, Ti, V, W and Cu. In the presence of more than 5% of Cu the test soln. must be filtered before extraction of the complex.

G. H. FOXLEY

2616. Rapid determination of cobalt in steel. F. Velasco Velasco and J. Hontoria y García Ortiz. *Inst. Hierro y Acero*, 1956, **9**, 176–182.—A simple method is described based on extracting the blue cobalt complex with thiocyanate without previous separation. Results can be obtained in < 1 hr. *Procedure*—Dissolve 0·1 g of sample turnings in H_2SO_4 (5 ml), H_3PO_4 (5 ml) and H_2O (10 ml); add HNO_3 (5 ml) and heat to avoid the formation of WO_3. Dilute the clear soln. with H_2O (20 ml), add conc. aq. NH_3 (10 ml) and dilute to 1 litre. To 10 ml of soln. add ammonium citrate (0·2 g) and centrifuge; add in succession Na_2HPO_4 (0·4 g), some crystals of KI and of $Na_2S_2O_3$, and NH_4SCN (0·3 g). Finally add $(NH_4)_2SO_4$ (2 g) and then, immediately *cyclo*hexanone (5 ml). Shake the closed tube violently for 1 min. and compare the extinction with a blank.   CHEM. ABSTR.

2617. The iodimetric determination of cobalt by the use of arsenate. G. B. Shakhtakhtinskiĭ and M. L. Turchinskiĭ. *Tr. Azerb. Ind. Inst.*, 1955, (11), 70–75; *Ref. Zhur., Khim.*, 1956, Abstr. No. 68,714.— To 10 ml of the cobalt soln. ($\simeq 0.05\,M$) add H_3AsO_4 soln. (50 ml) and 30% acetic acid (20 ml), and dilute to 50 or 60 ml. Heat to boiling-point and add aq. NH_3 dropwise until the NH_3 can be smelt (pH 7 to 8). Then add ethanol (40 ml), filter after 5 min. and wash the ppt. with 33% ethanol ($\times 5$) and with warm water ($\times 5$). Dissolve the ppt. of $Co_6(NH_4)_3(AsO_4)_5$ in 25 ml of H_2SO_4 (1:2·5), and to the arsenate soln. add benzene (25 to 40 ml), N KI (3 ml) and water (25 ml), and titrate with 0·1 N $Na_2S_2O_3$ until the organic layer is colourless. The described method is useful for the analysis of Fe - Co alloys. Dissolve the sample (1 g of turnings) in a small quantity of conc. HCl. Add 1 or 2 ml of conc. HNO_3 and evaporate to dryness. Dissolve the residue in water and make up to 100 ml. Neutralise an aliquot with aq. NH_3 to a permanent cloudiness and clear the soln. with one or two drops of conc. HCl. Dilute to 50 or 60 ml and add 2 ml of ammonium acetate, followed by acetic acid to a concn. of 4 or 5%, to give a total vol. of 150 ml. Add to the hot soln. a three to five-fold excess of H_3AsO_4 and boil for 5 to 8 min. Filter off the ppt. of iron arsenate and wash it ($\times 10$) with hot 3% acetic acid. Evaporate the filtrate and wash liquors to a vol. of 30 to 50 ml, add 0·5 N H_3AsO_4 (3 to 5 ml), dilute to 60 ml, warm and determine Co as above.   C. D. KOPKIN

2618. Determination of cobalt and iron in stellite using perchloric acid. A. M. Vovsi and F. M. Dobrovol'skaya. *Trudy Leningr. Metal. Zavod.*, 1955, (2), 116–118; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,846.—In analysing stellite, separate Cr from Co and Fe by oxidation with $HClO_4$ to fuming ($203°$ to $205°$) and subsequent distillation of

CrO_2Cl_2. Determine Co by electrolysis in ammoniacal soln. containing SO_4^{2-}. After separation as $Fe(OH)_3$, determine Fe with dichromate, with molybdosilicic and phenylanthranilic acids as indicators.   C. D. KOPKIN

2619. Iodimetric determination of nickel using arsenate. G. B. Shakhtakhtinskiĭ and M. L. Turchinskiĭ. *Trudy Azerb. Ind. Inst.*, 1955, (11), 64–69; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,843.— In analysing Fe - Ni alloys, precipitate Ni as $Ni_6(NH_4)_3(AsO_4)_5$ and determine AsO_4^{3-} by iodimetric titration after solution of the ppt. in H_2SO_4. Remove Fe by a preliminary pptn. with H_3AsO_4 in 4 to 5% acetic acid. *Procedure*—Dissolve 1 g of the alloy by warming with conc. HCl, evaporate almost to dryness with 2 ml of conc. HNO_3, dissolve the residue in water and make up to 100 ml. To an aliquot add water (50 ml), N ammonium acetate (2 ml) and acetic acid to a concn. of 4 to 5% (total vol. 150 ml). Warm to between 40° and 50°, add a three- or four-fold excess of warm H_3AsO_4, boil for 10 min. and immediately filter through a crucible of porosity 3 or 4. Wash the iron arsenate ppt. ten times with 3% acetic acid. Evaporate the filtrate and wash liquor to dryness, treat the residue with conc. aq. NH_3, add 0·5 N H_3AsO_4 (10 ml), N ammonium acetate (5 ml), and an excess of 15% aq. NH_3 (till the ppt. dissolves), then dilute to 50 or 60 ml, boil for 8 or 10 min., add ethanol (25 ml) and filter after 5 min. through a crucible of porosity 3 or 4. Wash the ppt. of $Ni_6(NH_4)_3(AsO_4)_5$ with ten portions of warm 66% ethanol containing two to three drops of aq. NH_3, and dissolve the ppt. in H_2SO_4 (1:2·5) (25 ml). To the soln. add C_6H_6 or $CHCl_3$ (20 to 25 ml) and N KI (3 ml), shake for a few sec., add water (25 to 30 ml), and titrate the liberated I with N $Na_2S_2O_3$ until the organic layer is colourless. The error is $\pm 0.08\%$ of Ni.

C. D. KOPKIN

2620. The determination, by radioactivation, of small quantities of nickel, cobalt and copper in rocks, marine sediments and meteorites. A. A. Smales, D. Mappin and A. J. Wood (A.E.R.E., Harwell, Berks., England). *Analyst*, 1957, **82**, 75–88.—The methods described for the determination of microgram or smaller amounts of Ni, Co and Cu involve neutron activation of the samples in the Harwell pile and radiochemical separation of their soln. in HCl (or, with meteorites and rocks, in mixtures of HCl, HNO_3, $HClO_4$ and HF, with subsequent fuming). The Ni is pptd. from ammoniacal soln. as the dimethylglyoxime complex and Cu from the filtrate as the thionalide. These compounds are dissolved separately and, after radiochemical purification, are pptd. as the Ni - dimethylglyoxime complex and CuSCN, respectively, and in these forms are counted against irradiated standards. The Co is separated as potassium cobaltinitrite and counted. The precision of the method is satisfactory and its accuracy has been checked by the analysis of standard steels. Results for standard granite G1 and diabase W1, some other rocks, commercial pure irons and seaweeds are quoted.

A. O. JONES

2621. The chemical separation and analysis of metallic compounds formed in certain nickel alloys. R. B. Golubtsova and L. A. Mashkovich. *Doklady Akad. Nauk, SSSR*, 1956, **106** (6), 1011–1014; *Ref. Zhur., Khim.*, 1956, Abstr. No. 68,752.—The conditions are studied for the separation of the phase Ni_3Ti in nickel alloys. Studies were made of

(a) double alloys of Ni and Ti containing 7·94, 10·8 and 12·94% of Ti, after heat treatment for 24 hr. at 1500°, cooling to 800° and maintaining this temp. for 100 hr.; (b) triple alloys with 18·92% of Cr and 8·38% of Ti, after heat treatment for 6 hr. at 1200°, 18 hr. at 1150°, 24 hr. at 800° and cooling in air; (c) the alloy EI-437 (20·5 of Cr, 0·35 of Si, 2·52 of Ti and 0·67% of Al) after ageing of the alloy at 800° for 250 to 2000 hr. The samples were cylindrical, of height 40 mm and diam. 15 mm. On the basis of the solubility curves of the phase of stoicheiometric composition Ni_3Ti and the double solid nickel soln. (with 5% of Ti) in various chemical media, and measurement of the difference of potentials of this pair, it was established that the best separation of the Ni_3Ti phase from Ni - Ti and Ni - Ti - Cr alloys was made in various electrolytes containing HNO_3. The use of a mixture of 1% HNO_3 and methanol is recommended. The anodic ppt. obtained on electrochemical solution of the samples are centrifuged off and dried in a current of H. Dissolve a known wt. of the ppt. in HCl - HNO_3, fume with H_2SO_4 and take up the residue in water. Determine Ni, Ti, Cr and Al in aliquots of the soln. The ratio of Ni to Ti in each anode powder corresponds to the theoretical in wt. and atomic percentages. X-ray-structural analysis shows that the separating phase has a hexagonal lattice. C. D. KOPKIN

2622. Determination of palladium by potentiometric titration in the presence of platinum. N. K. Pshenitsȳn and S. I. Ginzburg. *Izv. Sektora Platinȳ, I.O.N.Kh., Akad.Nauk, SSSR*, 1955, (32), 31–37; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,847.—The potentiometric titration of a soln. of a complex palladium chloride (**I**) in 0·15 to 0·3 N H_2SO_4 by a soln. of KI is carried out at room temp. in an atmosphere of CO_2, with a palladium electrode as the indicating electrode. Beginning with a definite concn. of $PtCl_6^{2-}$ in **I**, a minimum is found on the titration curve, the position of which defines the end-point of the titration. Increase of the content of Pt renders the minimum less clear, and the error in the titration of **I** increases. If the content of Pt is a few times greater than that of the Pd, then it is impossible to determine the Pd. In such cases the Pt is removed by pptn. as K_2PtCl_6, by the addition of K_2SO_4. The ppt. does not interfere in the titration. The error in the determination of 20 to 72 mg of Pd by the described method does not as a rule exceed 2%. The same accuracy is attained by determining Pd in the presence of Pt by the "rapid" titration method. which is based on the difference in the rates of the interaction of the complex palladium and platinum chlorides with KI. With $PtCl_4^{2-}$, KI reacts much more slowly than with **I**. In this method the titration is carried out as rapidly as possible, without waiting for a const. value of potential. C. D. KOPKIN

2623. Colorimetric determination of palladium with oximes. V. M. Peshkova, V. I. Shlenskaya and A. I. Rashevskaya. *Izv. Sektora Platinȳ, I.O.N.Kh., Akad. Nauk, SSSR*, 1955, (32), 61–74; *Ref. Zhur., Khim.*, 1956, Abstr. No. 61,848.—The palladium compounds with dimethylglyoxime (**I**), methylglyoxime (**II**) and salicylaldoxime (**III**) are sol. in non-aq. solvents. The yellow soln. formed by **II** or **III** in C_6H_6 or $CHCl_3$ have large values for the mol. coeff. of light absorption, which makes them suitable for the photometric determination of Pd without preliminary removal of accompanying elements. The compounds are extracted at pH 1 to

4 in the presence of excess of **II** or **III**. The same result as with **III** is obtained if to the soln. of the palladium salt is added salicylaldehyde (**IV**) and then hydroxylamine (**V**), although on simply mixing **IV** and **V** in the absence of Pd, **III** is not formed. To determine Pd colorimetrically, to the weakly acid soln. add a five- or six-fold excess of **IV** and a 10- or 15-fold excess of **V** (as compared with Pd), warm for 2 min. at 60° to 70° and, after cooling, extract the ppt. with C_6H_6. On adding to a soln. of Pd^{2+} a two- or three-fold excess of 1 : 2-naphthaquinone (**VI**) and then a 50-fold excess of **V** at pH 0·65 to 3·7, there is formed an intramolecular salt of 2-nitroso-1-naphthol, of composition $Pd(C_{10}H_6NO_2)_2$, which is completely extracted with $CHCl_3$; excess of **VI** is removed from the non-aq. layer by washing with alkali. By the use of this reaction it is possible to detect 0·038 μg of Pd per ml. The reaction may also be used for the colorimetric determination of 5 to 30 μg of Pd in soln. of its pure salts, and in the presence of Co, Cu, Ni, Fe, Pt^{4+} and Ir^{4+}. The relative error in the determination of Pd in a mixture with these elements does not exceed 5%. C. D. KOPKIN

2624. Bismuthiol II as an analytical reagent. III. Estimation of palladium. Anil Kumar Majumdar and Madan Mohan Chakrabartty (Jadavpur Univ., Calcutta). *Z. anal. Chem.*, 1957, **155** (1), 1–6 (in English).—With Pd, bismuthiol II forms an insol. red complex, $Pd(C_6H_5N_2S_3)_3$, which is stable in the presence of acids, ammonia, alkali, tartrate, citrate and EDTA (disodium salt) and at temp. up to 250°. With this reagent Pd can be estimated and separated from almost all other ions by pptn., either from 0·1 N acid or in the presence of one or more of the ions referred to above to keep interfering ions in soln. Silver, Hg^{2+} and Pb may be complexed with KI at pH 6 to 8; Tl^+ and Ag^+ may be separated in the presence of CN^- in an acetate buffer, when Pd remains in soln. and can be re-pptd. The concn. limit for detection is 0·01 μg per ml and for pptn. 0·3 μg per ml.

IV. Estimation of platinum metals. Anil Kumar Majumdar and Madan Mohan Chakrabartty. *Ibid.*, 1957, **155** (1), 7–10 (in English).—In the presence of mineral acid, bismuthiol II gives coloured ppt. with all the platinum metals. Palladium can be separated from Ru^{3+}, OsO_4^{2-}, Os^{4+}, Ir^{4+} and Rh^{3+} at pH 6·6 to 8 in the presence of EDTA (disodium salt), and from Au^{3+}, OsO_4^{2-}, Os^{4+} and Ir^{4+} at pH 6 to 7 with thiosulphate as complexing agent. Palladium can be separated from Pt either by retaining the Pt in soln. with tartrate at pH 6 to 8, or by retaining the Pd in soln. with cyanide at pH 5 to 6·5. G. BURGER

2625. Comparison of some methods for the determination of trace impurities in semi-conductors. A. A. Smales (A.E.R.E., Harwell, England). *J. Electronics*, 1955, **1** (3), 327–332.—The methods discussed are emission spectroscopy, mass spectroscopy (vacuum spark and isotope dilution), polarography, vacuum fusion, colorimetry and fluorimetry, the use of radioactive tracers and radioactivation (activating elements by neutron irradiation). The advantages and disadvantages of each method are mentioned. PHYS. ABSTR.

2626. Rapid orientation determination of small amounts of silica in ceramic clays by means of differential thermal analysis. E. Kanclíř (Inst. Acad. Science, Bratislava, Czechoslovakia). *Chem. Zvesti*, 1956, **10** (2), 116–119.—A rapid determination of

silica in ceramic clays of kaolin type, in amounts > 5%, is described. It is based on the reversible change of β-quartz into α-quartz during cooling. The differential thermal analysis curve is registered with a galvanometer of high sensitivity.

J. PELIKÁN

2627. Organic matter in clays. W. E. Worrall. *Trans. Brit. Ceram. Soc.*, 1956, **55** (11), 689–705.— The bitumen content is determined by the direct extraction of 25 g of clay with 200 ml of *n*-propanol for 8 hr. in a Soxhlet apparatus. The extract is distilled down to 25 ml, evaporated to dryness on a water bath and dried over silica gel in a vacuum desiccator. The lignin - humus content is deter-mined as the loss of wt. when 1 g of clay is digested at 80° with 25 ml of 20-vol. H_2O_2.   J. A. SUGDEN

2628. Spectrographic analysis of open-hearth slags by the copper cup-electrode solution method. I-Djen Ho and Shih-Cho Li (Inst. Metal Res., Acad. Sinica, China). *Acta Chim. Sinica*, 1956, **22**, 55–65.—An activated a.c. arc (IIC-39) was used as light source, and Sn (as $SnCl_2$ soln.) rather than Cr was used as internal standard since Si and Ca may thus be more satisfactorily estimated. Potassium bromide was added to the HNO_3 soln. of the sample for stabilisation of the arcing. The size and shape of the cup-electrode were so chosen that the height of the soln. surface did not vary much during exposure. A copper cup-electrode of 21 mm in diam., 11 mm in height and of approx. 2 ml in vol. (thickness of wall and bottom being 1·5 and 3 mm) was suitable. Because of the non-uniform dis-tribution of the elements to be analysed in the arc column, the slit was illuminated directly from the arc without using lenses. Ratios of Ca to Si in 20 slag samples were determined by reference to standard curves. The differences between spectro-graphic and chemical results were within ± 5% of the mean. Analyses for Si, Fe, Mn, Mg, Al and Ca in four slag samples of known composition gave satisfactory results.   S. H. YUEN

2629. Chemical analysis of a soda - boric oxide - alumina - silica glass of high silica and boric oxide content, described as Standard Glass No. 2. Chem. Analysis Committee, Society of Glass Technology. *J. Soc. Glass Tech.*, 1956, **40**, 53T–65T.—Details are recorded for the procedures previously described (*Ibid.*, 1950, **34**, 305T), but a modified method for B_2O_3 is based on back-titration with 0·05 N NaOH to bromothymol blue in the presence of mannitol. The B_2O_3 equiv. of the NaOH soln. is evaluated with a fused mixture of SiO_2, Na_2CO_3 and a known amount of pure borax. A standard deviation of 0·06% was achieved on a B_2O_3 content of 12·86%.   J. A. SUGDEN

2630. Differential thermal analysis and thermo-gravimetry applied to potassium perchlorate - aluminium - barium nitrate mixtures. V. D. Hogan, S. Gordon and C. Campbell (Pyrotechnics Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 306–310.—Thermogravimetric data show that $Ba(NO_3)_2$ catalyses the decomposition of $KClO_4$ to KCl, the decomp. temp. falling from $\simeq 600°$ to 520°. By combining these data with those from differential thermal analyses of binary and tertiary mixtures of the components, a rapid analysis can be made of the standard 3 : 4 : 3 mixture of $KClO_4$ - Al - $Ba(NO_3)_2$ used in pyrotechnics. For a const. wt. (4 g) of sample the area under the transition peak (rhombic → cubic) at 300° is

directly proportional to the percentage of $KClO_4$ present. The KCl and $Ba(NO_3)_2$ can be quant. removed from the Al, after ignition of the mixture at the predetermined temp., by extraction with water followed by filtration. The $Ba(NO_3)_2$ can be determined by difference or titration of Ba^{2+}. The loss on ignition represents the quant. decomp. of $KClO_4$ to KCl and is equiv. to the percentage of $KClO_4$ in the sample. The accuracy for each component is within ± 0·5%, but for the semi-quant. determination of $KClO_4$ from measured peak-areas the accuracy is only ± 5%.

W. J. BAKER

See also Abstracts 2474, 2475, 2476, 2477, 2479, 2483, 2485, 2488, 2494, 2793, 2816, 2817, 2835.

3.—ORGANIC ANALYSIS

2631. Catalyst for oxidative reactions. J. Körbl. Czech. patent 85,465; date appl. 1.12.55.—The product of the thermal decomposition of $AgMnO_4$, having a probable composition of $8Ag_2O.15MnO_2$.MnO_3, catalyses at 400° to 450° the oxidation of numerous org. and some inorg. compounds. This catalyst is useful as a filler for combustion tubes for elementary organic analysis. (*Cf. Anal. Abstr.*, 1957, **4**, 910.)   CHEM. ABSTR.

2632. New volumetric methods in analysis of organic compounds. III. Oxidation with chloramine [T]. A. Berka and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Československ. Farmac.*, 1956, **5** (6), 335–339.—Direct potentio-metric titration with chloramine T is possible in the presence of KBr for *p*-nitrophenylhydrazine, 2:4-dinitrophenylhydrazine, isoniazid, semicarbazide, thiosemicarbazide and thiourea (in acid soln.). In alkaline soln. (NaOH), salicylaldehyde, vanillin, furfuraldehyde, cinnamaldehyde and thiopentone are oxidised with chloramine T and the excess of the reagent is determined iodimetrically. The method can be used for all compounds containing

a —NH—C=S group.   J. VOLKE

2633. Analysis of binary liquid mixtures by molecular refractivity. P. S. Santos and F. W. Lima (Polytech. School, Univ. of São Paulo, Brazil). *An. Ass. Brasil. Quim.*, 1952, [1956], **11**, 73–80.— The determination of the percentage composition of binary liquid mixtures was studied by direct measurement of the refractive index and the density. A given formula was tested with mixtures of octyl and propyl alcohols, $CHCl_3$ and acetone, $CHCl_3$ and *iso*butyl methyl ketone, etc. Errors in the determination were, in general, low.

H. PRITCHARD

2634. Coulometry combined with gas-phase chromatography for the analysis of volatile mixtures. A. Liberti and G. Cartoni (Ist. di Chim. Generale e Inorganica, Univ. Roma, Italy). *R.C. Accad. Lincei*, 1956, **20**, 787–794.—The procedure consists in passing the various constituents, separated by a chromato-graphic column, through a combustion tube and de-termining the CO_2 produced by the different fractions by the coulometric - potentiometric method of Oelsen *et al.* (*Arch. Eisenhüttenw.*, 1951, **22**, 225). The apparatus is illustrated and described. The method has been used for the determination of the constituents of mixtures of aliphatic alcohols and of fatty acids.   P. HAAS

2635. Micro-determination of active hydrogen in organic compounds by lithium aluminium hydride. Z. Štefanac (The Univ., Zagreb, Yugoslavia). *Croat. Chem. Acta*, 1956, **28** (4), 295–297 (in English).—A procedure is outlined for determining active H by the Zerewitinoff method (*Ber. dtsch. chem. Ges.*, 1914, **47**, 1659, 2417) with 0·15 M LiAlH$_4$ in n-butyl ether in place of Grignard reagents. The sample (dried over P$_2$O$_5$ *in vacuo*) is placed in the reaction vessel of a Šoltys apparatus (*Mikrochem.*, 1936, **20**, 107), which is then flushed with dry N. The remaining operations are as described previously by Hochstein *et al.* for similar procedures (*J. Amer. Chem. Soc.*, 1949, **71**, 305; *Mikrochem.*, 1950, **35**, 400). W. J. BAKER

2636. Spectrophotometric microtechnique for the determination of sulphur in organic compounds. C. Bergamini and M. Maltagliati (Anal. Chem. Inst., Florence Univ., Italy). *Sperimentale*, 1956, **6** (4–6), 65–71.—The conditions of formation of methylene blue in an alkaline sulphide medium are studied, from the point of view of the micro-determination of S in organic bases by colorimetric absorption at 735 to 660 mμ. The sample is decomposed with Na in a sealed Pyrex-glass tube, in a metal bomb. Methylene blue is formed in the presence of Zn acetate in a Treadwell - Mayer apparatus. The Beer - Lambert law is followed between 0·2 and 1·0 μg of S per ml. Substances containing S in different states of oxidation, such as benzylpenicillin, have been examined. C. A. FINCH

2637. Analytical chemistry. Determination of C-methyl groups. Analytical possibilities. J. Calderón Martínez. *Quim. e Ind., Bilbao*, 1956, **3** (2), 56–58.—Methods and apparatus for the determination of C-methyl groups in organic compounds by chromic acid oxidation followed by titration of the acetic acid produced, and the effect of structure on the yield of acetic acid are reviewed. (14 references.) G. H. FOXLEY

2638. Determination of carbonyl value. M. Barro-Raffel and G. Jacini (Stazione Sperimentale Olii e Grassi, Milan). *Olii Min.*, 1956, **33** (11), 381–384.—A modification of the Terent'ev method is described, with improvements in speed and precision. Excess of phenylhydrazine is titrated potentiometrically and special precautions are observed. Details of technique and apparatus are given. The method is applied to a series of aldehydes and ketones, with an average error of $\simeq$ 0·6%. The method is suitable for the determination of volatile substances in rancid butters. C. A. FINCH

2639. Paper chromatography of 2 : 4-dinitrophenylhydrazones of aliphatic carbonyl compounds. F. Klein and K. de Jong (Unilever Res. Lab., Vlaardingen, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1956, **75** (9–10), 1285–1288 (in English).—The 2 : 4-dinitrophenylhydrazine derivatives of aliphatic carbonyl compounds having seven or more carbon atoms can be separated on paper impregnated with liquid paraffin, the mobile phase being dioxan - water. The reproducibility of R_F values is not particularly good, but individual spots can be identified by measuring their spectra directly on the paper with Tennant's apparatus (*cf. Anal. Chem.*, 1951, **23**, 1748). *Procedure*—Steep a strip of Whatman No. 1 paper once in a soln. of liquid paraffin in light petroleum (15 to 20%) and allow to dry. The carbonyl compounds are added in CHCl$_3$ soln. and developed by an ascending phase of dioxan and water (4 : 1). G. S. ROBERTS

2640. Chromatographic separation of readily volatile gases. K. Wencke (Inst. Catalysis Res., Ger. Acad. Sci., Berlin). *Chem. Tech., Berlin*, 1956, **8** (12), 728–730.—Descriptions are given of a gas chromatographic method and a specially designed apparatus for the rapid ($\simeq$ 10 min.) analysis of small samples (3 to 10 ml) of permanent gases (N, CO, CO$_2$, CH$_4$, H, etc.). The carrier gas technique is used for adsorbing the sample at 20° in a column of activated C (pre-activated by heating to 350° under vacuum); the column is fractionally desorbed to obtain fractions of individual permanent gases; and the amount of the permanent gas in each binary mixture of gas fraction and carrier gas is determined by measurement of the thermal conductivity of the binary mixture (method described). Industrial applications of the method include estimations of (*a*) CO and CH$_4$ in gas mixtures before and after catalytic hydrogenation of CO to CH$_4$, (*b*) N, CO and CH$_4$ in town's gas, and (*c*) N and CO in brown-coal carbonisation gas. The apparatus includes a special means for measuring the carrier gas stream, and several features render it especially suitable for rapid series analyses. H. L. WHITEHEAD

2641. Determination of trace amounts of carbon monoxide in gaseous hydrocarbons. K. H. Nelson, M. D. Grimes, D. E. Smith and B. J. Heinrich (Phillips Pet. Co., Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 180–183.—The method is based on the reaction of CO in methane with heated I$_2$O$_5$ to form CO$_2$ and I. Methane does not react with the I$_2$O$_5$ but other hydrocarbons do; these are removed by adsorption on activated charcoal, after low-temp. fractional distillation of the CO from the sample into a methane fraction. The liberated iodine is collected in a KI soln. and is measured spectrophotometrically. The accuracy is within $\pm$ 2 p.p.m. for up to 100 p.p.m. of CO. G. P. COOK

2642. Determination of small quantities of alcohols as coloured esters. Choice of *p*-sulphamylphenylazosalicylic [acid] esters. M. Pesez (Service de Recherches, Roussel-Uclaf, Paris-Romainville, France). *Ann. Pharm. Franç.*, 1956, **14** (7–8), 555–558.—Coloured esters of 5-(*p*-sulphamylphenylazo)salicylic acid (**I**) (preparation described) are made by condensation with alcohols. Ketones and esters do not interfere; glucose and lactose give a weak reaction; and phenols and aliphatic amines interfere. Of the steroids, only the hydroxyl compounds react. The absorption at 425 mμ obeys Beer's law between 10 and 50 μg of ethanol, and between 50 and 500 μg of certain steroids, including cholesterol. *Procedure*—Dissolve 0·02 g of **I** and 0·04 g of toluene-*p*-sulphonyl chloride in 1 ml of pyridine and set aside for 30 min. Introduce the sample dissolved in 0·5 ml of pyridine and heat on a boiling-water bath for 10 min. Add 0·5 ml of water and heat for a further 5 min. at 100°, then cool. Add 1 ml of ethanolamine. Extract with 2-ml portions of CHCl$_3$, wash the combined org. phases with 5 ml of water, and separate. Add 1 ml of ethanol, make up to 10 ml with CHCl$_3$ and determine the absorption against a blank. E. J. H. BIRCH

2643. Simple catalytic method for the estimation of ethanol. E. Pfeil and H.-J. Goldbach (Inst. für gericht. und soziale Med., Univ. Marburg a. d. Lahn, Germany). *Klin. Wochschr.*, 1957, **35** (4), 191–192.—The ethanol to be determined is oxidised to acetaldehyde by passing it in a current of air over a copper spiral heated to 280°. The acetaldehyde is absorbed in a soln. of 0·85% sodium nitroprusside and 8% morpholine in 0·1 N HCl, and the blue colour is measured in a colorimeter.

H. F. W. KIRKPATRICK

2644. New solvent for copper oxide and its application to the spectrophotometric determination of reducing sugars. F. Andreini and V. Vignolo (Dogane and I.I., Genoa, Italy). *Ann. Chim., Roma*, 1956, **46** (11), 920–928.—In this method for the spectrophotometric determination of reducing sugars, a mixture of aq. NH_3 and $(NH_4)_2S_2O_8$ is used as solvent for Cu_2O. The reduction of Fehling solution, filtration and solution of the Cu_2O in the new reagent takes about 1 hr. The method is as precise as the electrolytic method, and is more rapid.

C. A. FINCH

2645. Polarography of sugars. W. G. Overend, A. R. Peacocke and J. B. Smith (Dept. of Chem., Birkbeck College, London). *Chem. & Ind.*, 1957, (4), 113–114.—A useful buffer of high decomposition potential, consisting of tetramethylammonium phosphate and phosphoric acid at pH 8·0, has been employed for the polarography of a variety of sugars and their methyl deriv. In the sugars studied, the wave heights were proportional to concn. over a wide range, and a tenfold increase of buffer concn. caused no change in wave height. The limiting currents given by the unsubstituted sugars studied were shown to be independent of the mercury-reservoir height, indicating that the limiting current of the sugar is not determined by the rate of diffusion to the mercury drop, but by the rate of transformation of the $\alpha\beta$ equilibrium mixture from ring to reducible form at the mercury surface. Methyl deriv. of two particular sugars were studied where this rate of transformation was sufficiently high to render diffusion the slowest rate-controlling process; in these cases the wave heights varied with the head of mercury. Results are quoted for a number of sugars and their methyl deriv., in terms of a bulk rate constant which can be related to limiting current per unit concn. An increase of temp. above about 30° increased the transformation rate enough to cause diffusion to become the slowest rate-controlling step.

G. S. ROBERTS

2646. *iso*Butyl methyl ketone as wide-range solvent for titration of acid mixtures and nitrogen bases. D. B. Bruss and G. E. A. Wyld (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 232–235.—*iso*Butyl methyl ketone is an excellent differentiating solvent throughout the range of acid strengths, and is also useful for differentiating aliphatic and aromatic amines. The large potential range provides for the potentiometric determination of relative acidity and for the resolution of mixtures of strong, weak and very weak acids.

G. P. COOK

2647. Oxidation of acetic acid to glyoxalic acid. Analytical application. M. Pesez and J. Ferrero (Services de Recherches, Roussel-Uclaf, Paris-Romainville, France). *Ann. Pharm. Franç.*, 1956, **14** (7–8), 558–561.—Acetic acid is oxidised at pH 4 with H_2O_2 - HIO_4 and the glyoxalic acid formed gives a red colour with phenylhydrazine, which is extracted with dichloroethane and the extinction measured. *Procedure*—Acidify 1 ml of the acetic acid soln. to pH 3·5 with H_2SO_4 and add 0·2 ml of 0·12% H_2O_2 and 0·2 ml of 0·05 N $NaIO_4$. Set aside for 5 min. at room temp., then add 2 ml of 1% phenylhydrazine hydrochloride soln. and leave for a further 4 min. Cool the soln. for 1 min. on ice, then add 7 ml of a cooled soln. made by mixing 40 ml of 2% $K_3Fe(CN)_6$ soln. with 100 ml of conc. HCl. Extract the colour with 3 ml of dichloroéthane, add 5 ml of acetone and measure the extinction after 2 min. at room temp. Beer's law is valid at 510 mμ for the range 50 to 200 μg. Other substances oxidisable to glyoxalic acid interfere. In the presence of substances oxidisable to formaldehyde, sodium bisulphite soln. is added before the phenylhydrazine.

E. J. H. BIRCH

2648. The determination of sodium laurate in sodium N-lauroylsarcosinate. D. C. Cullum (Colgate - Palmolive Ltd., 371, Ordsall Lane, Manchester, England). *Analyst*, 1957, **82**, 120–122.—The Na N-lauroylsarcosinate (which may contain up to 3% of Na laurate formed during manufacture) is dissolved in water, the soln. is acidified with HCl, the free acids are extracted with ether, the extract is evaporated to low bulk and the vol. is adjusted to 100 ml with ether. The soln. (10 ml) is passed through a column of chromatographic kieselguhr impregnated with an alkaline phosphate buffer, and elution of the column is continued with ether. Fractions (10 ml) are collected and each fraction is evaporated to dryness, the residue is dissolved in neutral ethanol and titrated to phenol red with 0·02 N NaOH. The first few fractions will require a drop of alkali, the middle fractions containing the lauric acid will require appreciable vol. of alkali and in the final fractions the titre will drop again to the blank value. The first few and last few fractions provide a mean blank correction. Application to synthetic mixtures indicated a recovery of 99% and an average error of 1·3%.

A. O. JONES

2649. Identification of organic compounds by spot tests. I. Oxalic acid. F. Feigl and D. Goldstein (Mineral Products Lab., Min. Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 131–132.—Place a drop of the solution to be tested on a tile with a drop of HCl (1:1) and a granule of zinc (about 0·4 g). After 5 min. withdraw any undissolved zinc, add a drop of phenylhydrazine hydrochloride soln. (1%), and place the tile in an oven at 110° for 5 min. Add a drop of conc. HCl and a drop of H_2O_2 (10 vol.) to the cooled tile; after 3 or 4 min. a rose colour appears. For very small quantities of oxalic acid it is necessary to compare the result with a blank. The limit of identification is 1 μg of oxalic acid.

II. Formic acid. F. Feigl and D. Goldstein. *Ibid.*, 1952, [1956], **11**, 133–134.—The identification is based on the reduction of mercuric salts by formates. Place a drop of acid, neutral or slightly alkaline test solution on a tile, add successively a drop of $HgCl_2$ soln. and a drop of acetate buffer soln. Allow the mixture to dry in an oven at 100°, cool and moisten the dry residue with a drop of water containing a small quantity of dil. aq. NH_3. A black spot appears. The limit of identification is 5 μg of formic acid.

H. PRITCHARD

2650. Determination of glycollic acid in used anti-freeze solutions. H. Green (British Cast Iron Res. Ass., Alvechurch, Birmingham, England). *Analyst*, 1957, **82**, 107–110.—Used antifreeze soln. of the inhibited ethanediol type contain glycollic acid or its salts and also sol., colloidal and pptd. iron compounds. The iron compounds catalyse the oxidation of ethanediol and must be removed by centrifuging with water and ZnO before determination of the glycollic acid. An aliquot of the supernatant liquid is mixed with activated cation-exchange resin Zeo-Karb 225, the mixture is filtered and the resin is washed with water. The filtrate containing the ethanediol, glycollic acid and possibly small amounts of $PO_4{}^{3-}$ from the inhibitor is treated with anion-exchange resin De-Acidite FF and the mixture is filtered. The filtrate and washings contain the ethanediol and are rejected. The glycollic acid is eluted from the resin with 80% H_2SO_4, and conc. H_2SO_4 is added to the eluate. An aliquot is treated with a 2:7-dihydroxynaphthalene reagent (prep. described) and heated in boiling water. The cooled liquid is suitably diluted with conc. H_2SO_4, and its extinction is measured at 535 mμ against a control. The method is designed for 0·002 to 0·04% of glycollic acid, but this range can be extended by increasing the original aliquot from the treatment with ZnO.   A. O. JONES

2651. Determination of acetic anhydride by direct titration. O. R. Gottlieb (Ornstein & Cia., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 99–104.—The determination of acetic anhydride by direct titration with 0·3 *N* oxalic acid in ethyl methyl ketone is carried out in the presence of pyridine, which not only catalyses the reaction but also serves as an indicator. *Procedure*—The sample (0·5 ml) is weighed into a 50-ml tube, 1 ml of pyridine is added and the mixture is titrated with oxalic acid solution until a permanent turbidity is formed. A blank titration is made with 0·5 ml of glacial acetic acid instead of the sample.   H. PRITCHARD

2652. Liquid scintillation counting of carbon-14-labelled organic nitro compounds. S. Helf and C. White (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 13–16.—The liquid scintillation counting technique offers considerable advantages over conventional methods of counting low-energy beta emitters when applied to radioactive materials which are volatile or explosive. However, some materials, such as ^{14}C-labelled organic nitro compounds, effect a quenching of the scintillation, resulting in reduced counting efficiency. This effect depends on the concn. of the nitro compound added and is quant. characteristic of the compound. It is due to absorption by the nitro compound of a portion of the light spectrum emitted by the scintillator. The greater part of this absorption takes place in the u.v. region of the spectrum. The introduction of certain secondary solutes to the scintillator has the effect of shifting the emission spectrum towards the longer wavelengths. As a result, the absorption due to the nitro compounds may be largely offset and high counting efficiencies obtained.   L. S. ADLER

2653. Chromatographic separation and identification of amines. M. Večeřa and J. Gasparič (Res. Inst. Organic Syntheses, Pardubice-Rybitví, Czechoslovakia). *Chem. & Ind.*, 1957, (9), 263.—Primary and secondary amines can be effectively separated by chromatography of the 3:5-dinitrobenzamides on Whatman No. 4 paper impregnated with formamide, with *cyclo*hexane or a mixture of *cyclo*hexane and benzene (1 + 1) as the mobile phase. The deriv. can be revealed by spraying with a 1% ethanolic soln. of 1-naphthylamine, followed by exposure to u.v. light or, with greater sensitivity (2 μg), by exposure for 10 min. to a mercury-vapour lamp, when the amides appear as deep-violet spots in daylight with a red fluorescence in u.v. light. The method is rapid, the solvent reaching 25 cm from the start in 90 min. Milligram amounts of the 3:5-dinitrobenzamide deriv. can also be separated by column chromatography on Al_2O_3, with a mixture of benzene and $CHCl_3$ (3 + 1) as eluting agent. Tertiary amines can be separated from primary and secondary amines since, unlike these two classes, they do not react quant. with 3:5-dinitrobenzoyl chloride.   W. J. BAKER

2654. Identification of organic compounds by spot tests. III. Ethylenediaminetetra-acetic acid. F. Feigl and D. Goldstein (Mineral Lab. Prod., Min. Agric., Rio de Janeiro). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 135–137.—The property of EDTA of preventing the pptn. of Ni as the dimethylglyoxime or Zn as the 8-hydroxyquinolinate is made use of. In two neighbouring depressions in a tile place a drop of nickel solution. To one add a drop of the solution to be tested and to the other a drop of water. To each add a drop of aq. NH_3 and a drop of dimethylglyoxime solution. If the solution contains a sequestrating agent, a red colour occurs only in the blank. A similar reaction with Zn 8-hydroxyquinolinate can be used.   H. PRITCHARD

2655. Determination of water in methanethiol and ethanethiol. G. Matsuyama (Union Oil Co. of Calif., Brea, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 196–198.—Three methods were studied. The Karl Fischer method gave high results owing to interference from the thiol, which could not be entirely eliminated by treatment with *iso*octane in the presence of BF_3, as suggested in the literature. The i.r. spectrophotometric method, in which the –OH absorption band at 2·8 μ was used, gave more satisfactory results. The third method is based on measurement of the temp. at which turbidity (due to water) appears when the thiol is cooled. Although the accuracy here is only $\simeq \pm 10\%$ at the 0·2% level, the method is useful for plant-control purposes.   G. P. COOK

2656. Reaction for colorimetric estimation of some phosphorus compounds. B. Gehauf, J. Epstein, G. B. Wilson, B. Witten, S. Sass, V. E. Bauer and W. H. C. Rueggeberg (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 278–281.—The method is based on the measurement of the yellow colour produced by the oxidation of amine bases, such as benzidine, by various organophosphorus compounds. The reaction has been applied to a number of phosphono- and phosphoro-halides, phosphoroanhydrides and phosphorophenoxides. With only slight modification of the procedure, selected anhydrides of carbon compounds, *e.g.*, phthalic anhydride, and carbonyl halides also respond. The method can detect as little as 1 μg of some nerve gases, and Sarin (*iso*propyl methylphosphonofluoridate) can be determined to within $\pm 5\%$ of the true value. The mechanism of the reaction is discussed.   G. P. COOK

2657. Detection and estimation of nerve gases by fluorescence reaction. B. Gehauf and J. Goldenson (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 276–278.—Nerve gases such as Sarin react with indole and sodium perborate to form a highly fluorescent soln. of indoxyl. The emitted fluorescence ranges from $\simeq$ 460 to 490 mμ. A linear relationship between Sarin concn. and fluorimeter readings was found and as little as 0·05 μg of Sarin in 10 ml of soln. may be determined.

G. P. COOK

2658. Identification of organic compounds by spot tests. VI. Organic arsenic compounds. F. Feigl and W. A. Mannheimer (Mineral Products Lab., Min. Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 145–146.—Two techniques are described. The less sensitive is based on the formation of brown silver arsenate, and the other, more sensitive, is based on the identification of iodine liberated from iodide by calcium arsenate. (*i*) A drop of test soln. is placed in a micro-crucible over CaO (1 mg) and evaporated to dryness at 110°. A drop of $AgNO_3$ soln. is added to the cooled crucible, and the brown colour of silver arsenate appears after a minute or two. The limit of identification is 60 μg of As. (*ii*) The sample is mixed with CaO and heated. To the cooled residue are added one or two drops of dil. H_2SO_4 and the crucible is again cooled. A drop of CdI_2 soln. containing starch is added, and a blue colour observed immediately, or after half a minute, indicates As in the absence of Sb. By this method As was identified at a level of 1·4 μg in phenylarsonic acid.

H. PRITCHARD

2659. Organotin - dithizone complexes. The colorimetric determination of diethyltin and triethyltin compounds. W. N. Aldridge and J. E. Cremer (Toxicology Res. Unit, Medical Research Council Lab., Carshalton, England). *Analyst*, 1957, **82**, 37–43.—Diethyltin and triethyltin are almost completely separated by extraction with $CHCl_3$ in the presence of a borate - EDTA (disodium salt) buffer soln. (pH 8·4); the diethyltin passes into the aq. phase and the triethyltin into the $CHCl_3$. When an aliquot of the aq. phase is mixed with a soln. of dithizone in $CHCl_3$ the diethyltin - dithizone complex is extracted, and since the triethyltin - dithizone complex has the same extinction as dithizone at 510 mμ the extinction at this wavelength is a measure of the diethyltin present. When the $CHCl_3$ layer of the original extraction is mixed with the dithizone soln. in the presence of the buffer soln., the triethyltin - dithizone complex is formed and extracted, and the reduction of the extinction of the dithizone at 610 mμ is a measure of the triethyltin present. The method described is based on these observations. The EDTA in the buffer soln. prevents interference by Cu^{2+}, Zn, Fe^{2+}, Fe^{3+}, Pb, Mn, Co and Sn^{4+}, but Hg^{2+} interfere.

A. O. JONES

2660. Identification of organic compounds by spot tests. IV. Salicylic acid and esters. F. Feigl and H. Blohm (Mineral Products Lab., Min. Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 139–141.—Salicylic acid and its esters can be recognised by a strong blue - violet fluorescence when exposed to u.v. light. It is possible to separate salicylic acid from other fluorescent compounds that may occur by forming the methyl or ethyl ester. These esters are sufficiently volatile even at room temperature to enable the gaseous phase to be utilised. The test is carried out by placing a drop of the test solution in a tube closed with a hollow stopper, and adding a drop of ethanol and a drop of conc.H_2SO_4. The tube is closed and placed for 15 min. in an oven at 130°. In the presence of salicylic acid, at the end of the stopper, which has previously been moistened with alkaline hydroxide, a drop is formed with a violet fluorescence. The limit of identification is 5 μg of salicylic acid. This method can be used for the identification of aspirin, etc. H. PRITCHARD

2661. Volumetric determination of *p*-coumaric acid. I. Brominetric method. M. R. Verma, K. C. Agrawal and S. D. Paul (Nat. Physical Lab., New Delhi). *J. Sci. Ind. Res., India, B*, 1956, **15** (10), 589–592.—The number of bromine atoms that react per mole of *p*-coumaric acid when it is treated with $KBrO_3$ - KBr in HCl depends on temp., acidity and excess of brominating agent. The value levels off to 12 when the acidity of the reaction mixture is maintained at 0·2 to 0·6 *N*, at a temp. of 40° and above, and with the brominating agent in approx. 300% excess. This can form the basis of a brominetric method for the assay of *p*-coumaric acid under the conditions outlined.

II. Ceratometric estimation. M. R. Verma, K. C. Agrawal and S. D. Paul. *Ibid.*, 1956, **15** (11), 636–637.—The method is based on the observation that when *p*-coumaric acid is treated with 100% excess of ceric sulphate, one mol. of the acid reacts with 30 mol. of the ceric salt. The percentage error is $\simeq$ 0·59.

O. M. WHITTON
I. JONES

2662. New colorimetric method for the determination of small amounts of tropic and mandelic acids and their esters. I. Simonyi and G. Tokár (United Pharm. and Foodstuff Factory, Budapest). *Magyar Kém. Foly.*, 1956, **62** (10), 348–351.—Tropic (**I**) and mandelic (**II**) acids and their esters (atropine, hyoscine, homatropine) (as solids) are nitrated for 15 min. (for **I**) or for 30 min. (for **II**) at 50° to 60° with a soln. of 20% KNO_3 in conc. H_2SO_4. On making the product alkaline with hot 18 to 20% NaOH, a colour develops in 30 min. This is estimated by using an S42, S47 or S50 filter in the Pulfrich photometer. The sensitivity is 50 to 60 μg of **I** per ml and 20 to 30 μg of **II** per ml. The probable error is $\pm$ 3%.

A. G. PETO

2663. Polarographic determination of dicyclohexylammonium nitrite. J. C. Chaudhuri, T. J. Joseph and K. S. Rajagopalan (Tech. Dev. Estab. Lab., Kanpur). *J. Sci. Ind. Res., India, B*, 1956, **15** (10), 585–588.—A polarographic method for the estimation of dicyclohexylammonium nitrite, in terms of its nitrite content, is described. It is applicable to other organic nitrites. The limiting current due to the reduction of HNO_2 formed from the organic nitrite in acid medium reaches the limiting value only in concn. of 0·1 *M* mineral acid in the supporting electrolyte. Addition of uranyl acetate (as activator) fails to produce this result at lower concn.

O. M. WHITTON

2664. Identification of organic compounds by spot tests. V. Secondary aromatic amines. F. Feigl and H. Blohm (Mineral Products Lab., Min. Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quím.*, 1952, [1956], **11**, 143–144.—Secondary aromatic amines can be identified by oxidising them to quinonoid derivatives. A small quantity of the material to be tested is placed in a micro-crucible with a drop of

conc. HNO_3. If the original material is a solution, a drop is dried in the crucible before adding the HNO_3. A blue colour appears of intensity dependent on the quantity of secondary aromatic amine. By this method it is possible to identify 0·25 μg of diphenylamine, 0·17 μg of diphenylbenzidine, and 0·5 μg of carbazole. H. PRITCHARD

2665. A method for the detection and determination of isoquinoline and quinoline in the presence of one another. P. M. Maitlis (Queen Mary Coll., Univ. of London). *Analyst*, 1957, **82**, 135–136.—If mixtures of quinoline and isoquinoline are nitrated with an excess of HNO_3 in the nitrating mixture both compounds can be nitrated practically to completion (96 and 99%, respectively). The cooled mixture of nitroquinolines is neutralised with aq. NH_3, extracted with $CHCl_3$ and, after removal of the $CHCl_3$, the residue is dissolved in ether and chromatographed on a column of alumina. Movement on the column is followed by means of a u.v. lamp placed very near the column. The nitroisoquinoline band remains almost stationary and the nitroquinoline band is eluted rapidly. The upper band is eluted separately with $CHCl_3$. The separation is repeated with both fractions until they are homogeneous. The accuracy of the method is within $\simeq \pm 1\%$ and the limits of determination are about 1% of isoquinoline in quinoline and 2% of quinoline in isoquinoline. Much smaller amounts of isoquinoline in quinoline can be detected.
A. O. JONES

2666. Polarographic determination of antioxidants in gasoline [petrol]. V. F. Gaylor, A. L. Conrad and J. H. Landerl (Standard Oil Co., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 228–232.—From 2 to 60 p.p.m. of butylaminophenol (**I**) or dibutylphenylenediamine in petrol can be determined in 30 to 45 min. by measuring the oxidation waves produced at a wax-impregnated graphite electrode (*cf. Ibid.*, 1957, **29**, 224) in a stirred soln. comprising the sample (25 ml) and 5 ml of an isooctane soln. of Ba naphthenate (0·5%, w/v), diluted to 50 ml with 0·2 M LiCl in isopropyl alcohol. The polarogram of a 25-ml portion is recorded between $-0·25$ and $+0·75$ V, with a silver - silver chloride cathode and a potential variation of 1·24 mV per sec. Interference with the wave of **I** by oxidisable impurities is eliminated by calculating i_d from the current measured at $+0·30$ V and corrected for residual current. The standard error of one determination is $\pm 9\%$; the reproducibility is similar. W. J. BAKER

2667. Determination of trace amounts of total nitrogen in petroleum distillates. G. R. Bond, jun., and C. G. Harriz (Houdry Process Corp., Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 177–180.—The petroleum sample is percolated through a small silica-gel column, to adsorb the nitrogen compounds. The column is then broken up into a Kjeldahl flask and the N is determined by the usual procedures. The concn. range is 1 to 1000 p.p.m. of N and the accuracy is within $\pm 5\%$. The method was applicable to all the principal N-containing components of petroleum, but unsatisfactory results were obtained with nitronaphthenes. G. P. COOK

2668. Determination of trace amounts of lead in gasolines and naphthas. M. E. Griffing, A. Rozek, L. J. Snyder and S. R. Henderson (Ethyl Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 190–195.—The two methods described are modifications of the dithizone colorimetric procedure. In one method, Br is used to convert tetraethyl-lead into inorganic lead ions via diethyllead bromide, and in the other diisobutylene and Br are added to the sample to produce HBr gas, which completes the decomposition of the tetraethyl-lead to inorganic lead ions. The Pb is measured spectrophotometrically in the first procedure and by visual colour comparison in the second. The concn. range is 0·5 to 10 μg of Pb and the accuracy and precision of both methods are within $\pm 0·01$ p.p.m. G. P. COOK

2669. Determination of organically bound chlorine in petroleum fractions with oxy-hydrogen burner. L. Granatelli [American Oil Co. (Texas), Texas City, U.S.A.]. *Anal. Chem.*, 1957, **29** (2), 238–241.—The Cl is converted into HCl by combustion of the sample in the flame of a Beckman oxy-hydrogen burner. The products of combustion are absorbed in water and the Cl^- are determined potentiometrically with $AgNO_3$. A standard deviation of ± 2 p.p.m. of added Cl (as DDT) in the range 10 to 100 p.p.m. was obtained from 25 determinations. G. P. COOK

2670. Determination of trace amounts of chlorine in naphtha. J. G. Bergmann and J. Sanik, jun. [Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1957, **29** (2), 241–243.—Organic chlorine is converted into Cl^- by lamp combustion or diphenylsodium reduction, the former technique being recommended for most naphthas. The Cl^- are measured by a colorimetric procedure based on the displacement of SCN^- from $Hg(SCN)_2$ by Cl^-; the SCN^- are determined as the complex with Fe^{3+}. The procedure can detect as little as 0·5 μg of Cl and is accurate to within 0·5 μg in the range 1 to 100 μg. The standard deviation is $\pm 0·1$ p.p.m. at the 4 and 8 p.p.m. level of added Cl as chlorocyclohexane. G. P. COOK

2671. Determination of oxygen-containing functional groups in blown asphaltic bitumens and similar substances. J. Knotnerus (Koninklijke Shell Lab., Amsterdam). *J. Inst. Petrol.*, 1956, **42**, 355–360.—Modifications of existing methods are described for the determination of org. acids, saponifiable matter, hydroxyl and carbonyl groups, as a means of following the chemical changes occurring in the blowing or ageing of bitumen. These four groups account for almost all the O present. *Hydroxyl value*—The sample (0·5 to 2 g) is dissolved in 10 ml of pyridine, and 2 ml of acetic anhydride - pyridine (1 : 9, v/v) is added. The solution is boiled under reflux (for 2 to 6 hr. for heavy oils and maltenes or 18 to 24 hr. for isolated asphaltenes), 10 ml of benzene and 20 ml of water are added to the boiling mixture and shaken thoroughly. The solution is cooled to room temp. and transferred to a beaker together with three washings each of 2·5 ml of water and 2·5 ml of benzene, and titrated potentiometrically to pH 9 under rapid stirring with $\simeq 0·1 N$ aq. NaOH. Blank determinations are performed, omitting in the first the acetic anhydride and in the second the sample. *Carbonyl value*—The sample (0·5 to 2 g) is dissolved in 10 ml of benzene, and 10 ml of isopropyl alcohol is added with 2 ml of a reagent made by dissolving 10 g of hydroxylamine hydrochloride in a mixture of 20 g of water and 70 g of isopropyl alcohol. For maltenes the solution is boiled under reflux for 4 hr. and for bitumens and asphaltenes for 18 to 24 hr. The cooled solution, with washings,

is titrated potentiometrically to pH 3·5 under rapid stirring with $\simeq 0\cdot1\ N$ aq. NaOH. A blank determination omitting the sample is carried out. The titration error may be 0·1 ml in a volume of 1 to 2 ml. *Saponification value*—The method used is a modification of ASTM D939. Bitumen (0·5 to 2 g) is dissolved in 30 ml of benzene and boiled under reflux (for 2 to 6 hr. for heavy oils and maltenes or up to 24 hr. for samples containing asphaltenes) with 20 ml of $0\cdot1\ N$ *iso*propanolic KOH in a flask closed with an Ascarite - CO_2 trap. The cooled solution is acidified with 25 ml of $0\cdot1\ N$ *iso*propanolic HCl, washed into a beaker with the ASTM titration solvent, diluted to 125 ml and back-titrated potentiometrically with $0\cdot1\ N$ *iso*propanolic KOH. Deviations for some asphaltene samples may be as much as $\pm 20\%$. *Acid value*—The determination is by the standard ASTM method. Infra-red spectroscopy indicates that the saponifiable matter consists almost entirely of esters; the proportion of lactones and acid anhydrides present is very small.   A. JOBLING

2672. Recommended method for the determination of naphthalene in coke-oven gas. British Coke Research Association (75, Grosvenor Street, London). *Rep. Brit. Coke Res. Ass.*, December, 1956, 11 pp.—The recommended procedure involves absorption in picric acid followed by iodimetric titration. According to the approximate naphthalene content of the gas, the following factors are adjusted before beginning a determination—(*i*) strength and temp. of absorbent, (*ii*) number and type of absorbing vessels, (*iii*) time and rate of gas flow, the criteria being the recovery of 0·1 g of naphthalene per determination and the reduction of extraneous error. The ppt. of naphthalene and indene picrates is filtered off, washed with dil. picric acid and dissolved by the addition of $0\cdot1\ N$ NaOH to a bromothymol blue end-point, giving, after blank correction, a measure of the total picrate content. Glacial acetic acid and standard Wijs soln. are then added, the soln. is kept in the dark for 20 min., KI soln. is added and the liberated iodine is titrated with $0\cdot1\ N\ Na_2S_2O_3$, with starch as indicator. The amount of $0\cdot1\ N$ soln. equivalent to the indene (unsaturated hydrocarbons) present is obtained by difference from a parallel blank determination. The difference between the $0\cdot1\ N$ NaOH and one-half of the $0\cdot1\ N\ Na_2S_2O_3$ titration is taken to represent the naphthalene present and, with other necessary corrections, is converted to grains of naphthalene per cu. ft. of gas. No indication is given of the accuracy which may be expected.
                    J. O. LAY

2673. Standardisation of methods of analysis of coal and coke. XVI. Determination of moisture content of "analysis" sample. A. Crawford (Central Lab., N.W. Div., Nat. Coal Bd., Manchester). *Fuel, Lond.*, 1957, **36** (1), 7–25.—The direct and indirect gravimetric methods, and the Dean - Stark distillation method with toluene, give results that agree well enough to justify their acceptance as international standards. The sample must be air-dried in the balance room and then well mixed. In the gravimetric methods, 1 to 2 g of coal, as a layer of $\not> 0\cdot2$ g per sq. cm in a silica or aluminium vessel with a ground-on lid for use during weighing, is heated at 105° to 110° for 1·5 to 3 hr. in a current of oxygen-free N, giving 5 to 15 changes of atmosphere per hr. For the distillation method, 50 to 100 g of coal is boiled with 200 ml of toluene until no more drops of water condense. Alternative

apparatus of German or Swedish design, though less convenient than that of Dean and Stark, merit further tests.

XVII. Determination of total sulphur in coal. (2). Strambi bomb-combustion method. P. J. Jackson (Central Electricity Res. Lab., Leatherhead, Surrey). *Ibid.*, 1957, **36** (1), 26–38.—As an alternative to the Eschka combustion in air, combustion in the bomb has been found satisfactory under the following conditions. The sample (0·5 g) mixed with 0·5 g of Eschka mixture of low ($\not> 0\cdot5$ g per ml) bulk density is placed in a wide (base diameter 2·4 cm) platinum crucible previously lined with 0·2 g of Eschka mixture, and burned in a bomb containing oxygen at 25 atm. and 5 to 10 ml of aq. ammonium carbonate soln. (10%). Alternatively, 1 g of sample may be used, and the crucible may be lined with rice paper instead of Eschka mixture. Sulphate is extracted from the alkaline residue by hot aq. H_2O_2 and determined by the $BaCrO_4$ titrimetric method, which is unaffected by any Ba present in the original sample.

XVIII. Determination of carbon in coke by Sheffield high-temperature method. H. C. Wilkinson (Brit. Coke Res. Ass., 74, Grosvenor St., London). *Ibid.*, 1957, **36** (1), 39–42.—The satisfactory procedure for coals and blast-furnace cokes gave low results for C with unreactive foundry cokes, probably because they reach their ignition temp. only in the last stages of pushing into the hot central zone of the combustion tube. Therefore cokes containing $< 0\cdot5\%$ of volatile matter, or having a critical air blast $> 0\cdot074$ cu. ft. per min., must be advanced in slower stages (1 step of $1\frac{1}{2}$ in., 8 of $\frac{3}{4}$ in., 1 of $1\frac{1}{2}$ in.) or they must have a faster current of oxygen (500 ml per min.).
                    A. R. PEARSON

2674. Estimation of "asphalt and resinous bodies" in brown-coal tar. R. Klimke (VEB Kombinat Otto Grotewohl, Böhlen). *Chem. Tech., Berlin*, 1956, **8** (12), 726–728.—In a modification of the method of DIN53663, the tar sample is dissolved in a mixture (**I**) of ethyl acetate and *cyclo*hexane (1:2), and the "asphalt and resinous bodies" are pptd. for gravimetric estimation by adding the solution to *n*-hexane (**II**). The procedure takes $\not> 1$ hr. and is more accurate than the standard method; the ppt. obtained is non-sticky, readily filtered off, and free from foreign substances. *Procedure*—The sample (3 g) in a beaker is warmed to $\simeq 50°$ on a water bath with 5 ml of **I** till completely dissolved; the solution is cooled to room temp. and added dropwise to 80 ml of **II**, the beaker being washed out with 5 ml of **II**. After 10 min., the product is filtered, with suction; the residue on the filter is washed with **II**, dried with suction, transferred to a watch-glass, dried for 10 min. at 90°, cooled in a desiccator, and weighed.
                    H. L. WHITEHEAD

2675. The estimation of carboxyl groups in pulps with Complexone. H. Doering (Zentrallab. der Aschaffenburger Zellstoffwerke). *Papier, Darmstadt*, 1956, **10** (7–8), 140–141.—Pulp was freed from cations by treatment with HCl soln. and then treated with Zn acetate. The Zn bound by carboxyl groups was determined by titration of the Zn acetate soln., before and after reaction with the pulp, with EDTA (disodium salt). Results with this method were compared with those obtained by using the method of Wilson (*Svensk PappTidn.*, 1948, **51**, 45).   M. F. C. LADD

2676. Identification of fibres blended with wool (binary mixtures only). British Standards Inst. (2 Park St., London). B.S. 2793 : 1956, 7 pp.— Microscopical examination is used first to confirm the presence of wool and one other fibre only. The presence or absence of secondary cellulose acetate and cellulose triacetate is then established by extraction with acetone and dichloromethane, respectively. The identity of other fibres is indicated by the behaviour of the extracted sample when burnt, and is confirmed by extraction of further samples with mineral acids. Silk, cotton, viscose rayon, cuprammonium, polyesters (Terylene), nylon, regenerated protein and acrylic fibres, and calcium alginate may be identified by this method. G. S. ROBERTS

2677. Quantitative analysis of intimate mixtures of secondary cellulose acetate with certain other fibres. British Standards Inst. (2 Park St., London). B.S. 2792:1956, 6 pp.—Secondary cellulose acetate is extracted from the mixture of fibres with acetone at room temp. and the residue is weighed. The method covers mixtures of secondary cellulose acetate with cotton, wool, nylon, polyesters and viscose rayon. G. S. ROBERTS

2678. The determination of the formaldehyde yield of cellulose textiles treated with formaldehyde, urea - formaldehyde or melamine - formaldehyde. W. J. Roff (B.C.I.R.A., Shirley Inst., Didsbury, Manchester). *J. Text. Inst., Trans.*, 1956, **47** (6), T309–T318.—The finish is hydrolysed by 12 *N* H_2SO_4 by standing overnight without heating and the yield of formaldehyde is assessed colorimetrically by means of chromotropic acid. N. E.

2679. Estimation of alcoholic constituents of essential oils. III. Benzyl alcohol - benzyl acetate system. R. C. Pant, S. Z. Arif and J. B. Lal (H.B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1954, [1955], **10**, 48–54.—The formulae proposed by Gildemeister and Cocking were checked by estimating benzyl alcohol in synthetic binary mixtures of benzyl alcohol and benzyl acetate. The Gildemeister formula gave considerable deviation from the experimental result, but that proposed by Cocking—

alcohol (%) $= (Mv_2 - v_1)/(561 \cdot 04 - 0 \cdot 42v_2)$, where M = mol. wt. of alcohol and v_1 and v_2 = ester values before and after acetylation, gave results accurate within 1%. S.C.I. ABSTR.

2680. Estimation of alcohols in essential oils. II. J. B. Lal, K. Narain and B. K. Jain (H.B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1954, [1955], **10**, 70–73.—Formulae are derived for the estimation (by ester-value determinations before and after acetylation) of individual alcohols in mixtures containing (*i*) two monohydric alcohols and (*ii*) two monohydric alcohols and an ester. Their application was experimentally verified with benzyl alcohol - 2-phenylethanol mixtures. S.C.I.ABSTR.

2681. Estimation of esters and alcoholic constituents [of essential oils]. III. A system consisting of two esters, one alcohol and one ketone. J. B. Lal, R. C. Pant and V. M. Patwardhan (H.B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1954, [1955], **10**, 74–88.—Formulae are derived for the estimation (by ester-value determinations before and after acetylation) of the two individual esters in a quaternary mixture of an alcohol, two esters

and a ketone, and are experimentally verified by results obtained by using mixtures of benzyl alcohol, santalyl acetate and benzyl acetate. S.C.I. ABSTR.

2682. Estimation of alcoholic constituents and esters in essential oils by formylation. III. Geraniol - benzyl acetate - phenylethyl acetate. R. C. Srivastava and J. B. Lal (H.B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1955, [1956], **11**, 28–30.—Results indicate that individual esters cannot be accurately determined by the methods and formula previously described (*cf. Anal. Abstr.*, 1957, **4**, 2681) when present in a mixture of two different esters and an alcohol if the ester-value difference is small. S.C.I. ABSTR.

2683. Estimation of alcoholic constituents in essential oils by formylation. II. S. M. Ahmed, M. C. Joshi and J. B. Lal (H. B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1955, [1956], **11**, 34–40.—The period of time necessary for the complete formylation of various primary, secondary and tertiary alcohols is established as 24 hr. at 25° to 30°, with the exception of benzyl alcohol which requires 48 hr. Prolongation of this period to a substantial extent does not appear to cause acetylation. S.C.I. ABSTR.

2684. Estimation of esters and alcoholic constituents in essential oils. VI. System consisting of two different alcohols, one ester, one ketone and an acid. J. B. Lal and A. K. Ghosh (H.B. Technol. Inst., Kanpur). *J. Proc. Oil Technol. Ass., India*, 1955, [1956], **11**, 75–78.—Formulae are derived for the estimation (by the acetylation procedure) of two different alcohols present in a system containing two alcohols with an ester, a ketone and an acid. S.C.I. ABSTR.

2685. Determination of the essential oil, ethanol and water content of Eau de Cologne and perfumes. A. Ady and L. Hunyady (Staatliches Kontroll-Lab. für die Pflanzenöl-Ind., Budapest). *Fette, Seif., Anstrichmitt.*, 1956, **58** (9), 768–769.—For the determination of essential oil, a sample of the perfume is diluted with water and extracted with ether. After being dried with Na_2SO_4, the ether extract is mixed with dibutyl phthalate as a fixative, and the ether is removed first by heating on an ethanol bath and finally by irradiation with an i.r. lamp at 34°. When the odour of ether has almost disappeared, the flask is weighed at 5-min. intervals and the wt. is plotted against time; the point at which the ether is completely removed is indicated by the intersection of two lines on the graph. The determination takes 6 hr. and the relative error is $\pm 0 \cdot 8$%. For the determination of ethanol, the sample is diluted with 2 *N* H_2SO_4 and the mixture is set aside for 30 min.; the oil which separates is decanted and the residual liquid is filtered through talc. The ethanol in an aliquot of the filtrate is determined by oxidation with a standard soln. of $K_2Cr_2O_7$. Water is determined by treating the sample with magnesium nitride (preparation described), the NH_3 evolved being determined acidimetrically. E. HAYES

2686. The identification of nylon and related polymers by paper chromatography. M. Clasper, J. Haslam and E. F. Mooney (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *Analyst*, 1957, **82**, 101–107.—The sample of polymer (25 mg) is hydrolysed with dil. HCl by heating at 120°

in a sealed tube overnight, and the appearance of the contents before and after the tube has cooled is noted. The contents, their odour being noted, are transferred to a beaker with 1 or 2 ml of water (any change effected by the addition of water being noted) and are evaporated to dryness once or twice with small additions of water to remove HCl, and are finally dried at 105°. The residue is warmed with ethanol and the presence or absence of insol. matter is noted. The ethanolic soln. is spotted in duplicate on chromatographic paper and the chromatogram is developed with n-propanol - aq. NH_3 - water for about 7 hr. The air-dried paper is finally dried at 105° and is examined in u.v. light. The two chromatograms are separated. One is sprayed with a ninhydrin reagent and dried in air and then at 105°, and the other is sprayed with a methyl red - borate buffer reagent and dried between filter-papers. A tabular scheme correlates the preliminary observations and the reactions in the chromatogram with the identity of nylon polymers and copolymers.   A. O. JONES

2687. Analysis of polyamides 66, 6 and 11 by means of paper chromatography. G. Poles and M. C. Peverati-Scandurra. *Tinctoria*, 1956, **53** (12), 509–514.—The monomolecular polyamide soln. are hydrolysed by means of H_2SO_4 to obtain a solid fraction consisting of adipic acid and of the sulphate of ω-amino-undecanoic acid and a liquid fraction containing the sulphates of hexamethylenediamine and of ε-aminocaproic acid. The solid fraction taken up in 98% formic acid soln. is deposited on filter-paper and the filtrate is chromatographed after acidification on an ion-exchange column. The products are eluted with a soln of n-propanol, conc. aq. NH_3 and water (60:30:10 by vol.).
                                          B.C.I.R.A. ABSTR.

2688. Changing frontiers in the analytical chemistry of paint materials. C. Whalley (Res. Ass. Brit. Paint, Colour and Varnish Mnfrs., Teddington, Middlesex). *J. Oil Col. Chem. Ass.*, 1956, **39** (3), 193–211.—The applications of new analytical techniques to the analysis of paint materials are reviewed. Developments in micro and semi-micro techniques, spot tests and colorimetric methods, the use of paper and vapour-phase chromatography and of ion-exchange resins, and applications of complexometric titrations are described. (31 references.)   N. E.

2689. Determination of phthalic anhydride in oleoglycerophthalic paints. L. David. *Chim. Anal.*, 1957, **39** (2), 61–62.—The paints examined comprised a mineral pigment, a binder (a mixed glycerol ester of phthalic anhydride and a fatty acid) and a diluent. The determination is based on Kappelmeier's method. The binder is extracted with ether by centrifuging and, after removal of ether by decantation and evaporation, the extract is boiled gently with a predetermined vol. of 0·5 N ethanolic KOH to precipitate K phthalate as the form crystallising with 1 mol. of ethanol. The ppt. is filtered off, washed, dried at 100°, and weighed.
                                          W. J. WRIGHT

2690. Photocolorimetric method of determination of diphenylguanidine in raw rubber mixes and vulcanisates. V. B. Stepanova. *Trudӯ Nauch. Issled. Inst. Rezin. Prom.*, 1955, (2), 190–193.—This method is based on the colour reaction of diphenylguanidine with Co oleate in a benzene medium. The diphenylguanidine is extracted with hot ethanol,

the extract is treated with ether and HCl; the acid extracts are made alkaline and treated with benzene. To the benzene soln. is added a soln. of Co oleate in benzene. The assessment is carried out from a calibration curve. The method is more accurate than the gravimetric or volumetric methods.
                                          RUBBER ABSTR.

2691. Photocolorimetric method of determination of thiuram (disulphides) in raw rubber mixes and vulcanisates. V. B. Stepanova. *Trudӯ Nauch. Issled. Inst. Rezin. Prom.*, 1955, (2), 194–199.—This method is based on the colour reaction of thiuram disulphide with $CoCl_2$ in an ethanol - benzene (7:3) medium. The thiuram is extracted with hot ethanol, the soln. mixed with benzene, the $CoCl_2$ soln. is added, the whole being treated with water, the ethanol - benzene mix is added and colorimetry applied. In another method the polymer is pptd. from the benzene soln. by ethanol, while the thiuram remains in the soln. to which there is added an ethanol soln. of $CoCl_2$. The result is assessed from a calibration curve or from an experimental formula. In vulcanisates thiuram is frequently converted into zinc dimethyldithiocarbamate, which also forms a coloured complex; this is determined by calcination of the acetone extract followed by determination of Zn in the ash.
                                          RUBBER ABSTR.

2692. Application of paper chromatography to the identification of accelerators and antioxidants [in rubber]. IV. Detection of antioxidants. J. W. H. Zijp (Rubberinst. T.N.O., Delft). *Rec. Trav. Chim. Pays-Bas*, 1956, **75** (9–10), 1129–1136 (in English).—Antioxidants containing an amino group are extracted from rubber mix or vulcanisate (5 g) for 8 hr. with hot acetone. The solvent is evaporated off and the residue is dissolved in 96% ethanol at its b.p. Impurities are filtered off and the filtrate is evaporated to small bulk, and applied to completely acetylated Whatman No. 1 paper. Benzene - 96% ethanol (1:1, v/v) is used as the mobile phase and a 4% soln. of benzoyl peroxide in benzene is a suitable colour-forming reagent. R_F values and identification limits of 14 antioxidants are given. Phenolic antioxidants are extracted as above, but three drops each of 20% $SrCl_2$ and 4 N aq. NH_3 are added to the ethanol soln. before filtering to precipitate paraffins and stearic acid, which interfere. The alcohol extract is separated on acetylated paper, with two mobile phases, *viz*, butyl acetate - pyridine - methanol - water (1:5:1:3) and *iso*-propyl alcohol - methanol - water (3:3:2). Colours are developed with Tollens reagent or Millon's reagent. Phenolic antioxidants cannot often be characterised with certainty. The separation on untreated paper of antioxidants coupled with diazotised arylaminosulphonic acids is described briefly; the method has only limited usefulness.
V. Detection of accelerators and antioxidants in rubber of unknown composition. J. W. H. Zijp. *Ibid.*, 1956, **75** (9–10), 1155–1158 (in English).—A detailed procedure is described for the identification of antioxidants and accelerators in rubber mixes and vulcanisates. Acetone extraction is followed by one or more purification stages. The final separations are carried out chromatographically on acetylated paper.   G. S. ROBERTS

2693. Extraction of nitroguanidine propellants with pentane - methylene chloride [dichloromethane] azeotrope. J. O. Watts and H. Stalcup (U.S. Naval Powder Factory, Indian Head, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 253–254.—The use of

dichloromethane as the extracting solvent results in a significant loss of the nitroguanidine component. An azeotrope of pentane-dichloromethane (2 to 1 by vol.) reduces the loss to an insignificant amount, even in the presence of an excessive quantity of water. G. P. Cook

See also Abstracts 2486, 2550, 2553, 2579, 2627, 2847.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

2694. Simultaneous determination of radiochemical mixtures [of sodium and potassium in blood]. A. S. Blum (Radio-isotope Service, Veterans Admin. Hosp., Coral Gables, Fla., U.S.A.). *Nucleonics*, 1956, **14** (7), 64–65.—Equilibrium is established between the exchangeable Na and K in the body and known amounts of ^{24}Na and ^{42}K in 24 to 40 hr. The radioactivity of samples of blood and either recently excreted urine or haemolysed red cells is measured and the Na and K concn. of the samples are determined with a flame photometer. The concn. of total exchangeable Na and K can then be calculated. G. J. Hunter

2695. Neutron activation analysis of tissue: measurements of sodium, potassium and phosphorus in muscle. L. Reiffel and C. A. Stone (Illinois Inst. Tech., Chicago, U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (2), 286–291.—In the method described, milligram amounts of tissue samples and inorganic standards are placed in screw-cap containers made of reactor graphite and subjected to neutron bombardment in a nuclear reactor. The induced radioactivity, which is almost entirely due to the formation of ^{42}K, ^{24}Na and ^{32}P, is then measured with a simple Geiger counter and scaler. Total γ-activity is counted through an aluminium absorber (1·7 g per sq. cm) and γ- plus β-activity (energy $> 1·75$ meV) through a thinner absorber (0·8 g per sq. cm). From the ratio of the counts for ^{24}Na and ^{42}K (determined from the standards) under these conditions the amounts of Na and K in the samples are calculated by two successive approximations. The content of P is determined from the β-activity remaining after eight days, by which time the ^{24}Na and ^{42}K are dead. The accuracy attainable is within about 5%. W. H. C. Shaw

2696. Polarographic estimation of potassium in biological materials. A. Heyrovský (Lab. II, Med. Clin., Charles' Univ., Prague, Czechoslovakia). *Vnitřní Lékařství*, 1956, **2** (3), 234–239.—Tissue is ashed in a platinum crucible and the ash is dissolved in dil. HCl. Blood serum is treated with trichloroacetic acid and filtered. Potassium is pptd. as the insoluble tetraphenylboron salt, the ppt. is dissolved in acetone, evaporated to dryness in a platinum crucible and ignited. Potassium is determined in the resulting KBO_2 by polarography in tetra-alkylammonium hydroxide as supporting electrolyte. (See also *Anal. Abstr.*, 1957, **4**, 375; and *Coll. Czech. Chem. Commun.*, 1956, **21**, 1150.) A. Heyrovský

2697. Spectrochemical determination of magnesium, chromium, nickel, copper and zinc in human plasma. R. Monacelli, H. Tanaka and J. H. Yoe (Dept. of Chem., Univ. of Virginia, Charlottesville, U.S.A.). *Clin. Chim. Acta*, 1956, **1** (6), 577–582.—The spectrography is carried out with graphite electrodes after the sample has been prepared as follows. Blood is collected as described by Thiers *et al.* (*Anal. Chem.*, 1955, **27**, 1725). To 8 to 10 g of plasma (3 to 3·5 g for red cells or whole blood) add 2 ml of redist. HNO_3 and 0·5 ml of 30% HNO_3, heat at slightly below b.p. to a syrupy stage, when heavy brown fumes are evolved. Lower the temp. to avoid "self-ignition" and after the reaction has subsided raise the temp. to bring the residue to complete dryness; place the flask in a muffle-furnace at 350° overnight. To the cooled residue add 1 ml of HNO_3 and boil slowly to dryness; repeat this operation. Cool, add 1 ml of conc. HCl and again boil to dryness. Add the internal standard to the residue and make up to 5 ml. Average values found for normal plasma in μg per g are Mg, 24; Cr, 0·18; Ni, 0·04; Cu, 1·2; and Zn, 1·3. H. F. W. Kirkpatrick

2698. An indirect flame-photometric method for calcium in plasma and urine. P. P. Poulos and R. F. Pitts (Cornell Univ. Med. Coll., New York, U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (2), 300–303.—In the method described, plasma and urine samples are treated with trichloroacetic acid, and the Ca in an aliquot of the supernatant fluid obtained by centrifuging is pptd. as oxalate. The ppt. is collected by centrifuging, washed once with dil. aq. NH_3, dissolved in HCl and diluted to known vol. The emission of this soln. at $422·7$ mμ is measured in a spectrophotometer with flame attachment. Recovery of added Ca from plasma and urine is complete, with a coeff. of variation of $\pm 1·57$ and $\pm 1·70\%$, respectively. Good agreement is found with results by a conventional gravimetric oxalate procedure. W. H. C. Shaw

2699. A method of plasma dialysis and its application to the determination of the diffusible fraction of calcium. P. P. Poulos (Cornell Univ. Med. Coll., New York, U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (2), 292–299.—Details are given of a simple viscose-tubing dialysis apparatus in which 4 ml of plasma sample is dialysed against 6 ml of buffered isotonic balanced salt soln., the pH of which can be accurately controlled. An examination is made of the percentage dialysable fraction of plasma Ca in relation to pH (7·0 and 7·4), total protein concn., and plasma calcium concn. by a flame-photometric method (*cf. Anal. Abstr.*, 1957, **4**, 2698). W. H. C. Shaw

2700. Spectrophotometric titration of serum calcium and magnesium. B. Zak, W. M. Hindman and M. Fisher (Dept. of Path., Wayne Univ. Coll. of Medicine, Detroit, Michigan, U.S.A.). *Amer. J. Clin. Path.*, 1956, **26**, 1081–1093.—The procedure is based on complexometric titration with EDTA, with murexide and Eriochrome black T as indicators, the end-point being determined spectrophotometrically. The value obtained for Ca is subtracted from the total milli-equiv. per litre to give the amount of Mg. R. S. Tonks

2701. Colorimetric method for the micro-determination of silicon in tissues. M. Antonielli (Ist. di Fisiologia Umana, Univ. Perugia, Italy). *R.C. Accad. Lincei*, 1956, **20**, 813–815.—In a review of the methods available for the determination of small quantities of Si in biological tissues, attention is drawn to the discordant results obtained. As the main difficulty encountered is due to the presence

of phosphate in the ash, a study has been made of the behaviour of aq. mixtures of the sodium or ammonium salts of molybdo-silicic and -phosphoric acids. It was found that whereas the molybdo-silicate (**I**) is formed in the cold and only attains its max. colour when heated at 50°, molybdophosphate (**II**) is pptd. at that temp. as yellow crystals. Further, **I** is formed at pH 1 to 1·2 and retains its colour even at pH 4, but **II** begins to form at pH 0·5 to 1 and its colour gradually decreases as the acidity is reduced; **II** is sol. in strongly alkaline soln. The determination of Si is therefore carried out by adding sodium or ammonium molybdate to the strongly acid sample soln. and heating at 50°; the pptd. **II** (kept at 50°) is filtered off, and the filtrate, which should be free from phosphate, is made slightly alkaline, to ensure non-interference from traces of **II**, and the yellow colour due to **I** is then determined colorimetrically, against a calibration curve. If the yellow colour is not sufficiently intense, owing to the small amount of **I** present, the **I** may be reduced to the corresponding blue compound by means of 4-amino-1-naphtholsulphonic acid and determined by colorimetry. The method has given consistent results with all the tissues examined.　　　　　P. HAAS

2702. An analytical procedure for the acid-soluble phosphorus compounds in rat-skeletal muscle. C. J. Threlfall (M.R.C. Lab., Woodmansterne Rd., Carshalton, England). *Biochem. J.*, 1957, **65** (4), 694–699.—A method is described for the determination of 95% of the phosphate compounds in a HClO₄ extract of tissue, *e.g.*, rat-skeletal muscle. The nucleotide components are adsorbed on Norit charcoal and are eluted with aq. pyridine before their separation by paper chromatography. After removal of inorg. P and creatine phosphate P as the molybdophosphoric acid complex, the glycolytic intermediates are pptd. as barium salts. After removal of Ba with Amberlite cation-exchange resin IR-120(H), the soln. are lyophilised and the compounds are separated by paper chromatography, and P is determined colorimetrically in the eluate from each spot.　　　　　J. N. ASHLEY

2703. The role of copper ions in the reduction of molybdophosphate by ascorbic acid and their application in the determination of inorganic orthophosphate. J. L. Peel and B. C. Loughman (Agric. Res. Council Unit for Microbiol., Univ. Sheffield). *Biochem. J.*, 1957, **65** (4), 709–716.—The reduction of molybdophosphate to a blue compound by ascorbic acid under the conditions described by Lowry and Lopez (*Brit. Abstr. C*, 1946, 286) is inhibited by metal-binding agents such as Na₂S, diethyldithiocarbamate, EDTA and cysteine. This effect is overcome by Cu²⁺, and a modification involving addition of $4·2 \times 10^{-6}$ M Cu²⁺ is described. With $1·7 \times 10^{-4}$ M Cu²⁺ the sensitivity of the method is increased by 50%, but the timing of the operations is more critical. Concn. of Cu²⁺ greater than $3·3 \times 10^{-4}$ M interfere.　　　　　J. N. ASHLEY

2704. Quantitative measurement of sulphur-35 in biological samples. R. K. Poddar (Biophysics Div., Inst. of Nucl. Physics, Calcutta, India). *Nucleonics*, 1957, **15** (1), 82–83.—The self-absorption coefficient for the β-radiation in dried blood is determined; this enables small samples to be used and 10^{-3} to 10^{-4} μC can be measured. The error due to sample preparation is ± 5%.　　　　　G. J. HUNTER

2705. The estimation of serum-protein-bound iodine by alkaline incineration. J. D. Acland (Dept. of Pharmacol. and Therapeutics, Univ. of Sheffield). *Biochem. J.*, 1957, **66** (1), 177–188.—A colorimetric method is described, suitable for routine use. The iodide which is formed after ashing the sample with alkali is determined by its catalytic effect on the reduction of ceric to cerous salts by As₂O₃. Twenty-three determinations on a sample of serum, with Zn(OH)₂ for the pptn. of the serum-bound iodine, gave an average value of 4·3 μg per 100 ml and a standard deviation of ± 0·17 μg per 100 ml. Analyses on ppt. obtained with trichloroacetic acid give inconsistent results because of difficulties in the ashing procedure. There is loss of iodine if the temp. of ashing is greater than 650°. Acidification of a suspension of the ashed protein also causes loss of iodine, but elution of the iodide from the ash with alkali is satisfactory. A linear calibration graph is constructed for the reaction between ceric salts and H₃AsO₃ which relates the concn. of added iodide to log of extinction measured at 415 mμ after the reaction has progressed for 12·5 min. The catalytic effect of the iodide is partly inhibited by Zn²⁺, and the inhibition is greater at high concn. of iodide.　　　　　J. N. ASHLEY

2706. The ultra-micro determination of total and protein-bound iodine. M. C. Sanz, T. Brechbühler and I. J. Green (Central Lab., Univ. Hosp., Geneva, Switzerland). *Clin. Chim. Acta*, 1956, **1** (6), 570–576 (in English).—The alkaline ashing method of Barker (*J. Clin. Endocrin. & Metabolism*, 1956, **10**, 1136) is adapted for use with 50 μl of serum, urine or saliva.　　　　　H. F. W. KIRKPATRICK

2707. Determination of protein-bound iodine in micro amounts of serum or plasma. J. Fischl (Malben Hosp., Beer Yaacov, Israel). *Clin. Chim. Acta*, 1956, **1** (5), 462–469.—Proteins in 0·1 ml of serum are pptd. with HClO₄ soln. and digested either by heating with HClO₃ containing a little CrO₃ or by incineration with Na₂CO₃. Colorimetry is carried out by the catalysis of the Ce⁴⁺ - As³⁺ reaction; brucine is added at the end of the reaction time and the soln. is heated in boiling water for 5 min. By this means the colour is stabilised and intensified.　　　　　H. F. W. KIRKPATRICK

2708. Spectrophotometric method for the determination of submicrogram amounts of nickel in human blood. M. L. Cluett (Univ. Virginia, Charlottesville, U.S.A.). *Dissert. Abstr.*, 1956, **16** (9), 1570.—The blood is ashed with HNO₃ and the mineral constituents are converted into chlorides. Iron and copper are separated from 7·0 to 7·5 M HCl soln. on Dowex-1 anion-exchange resin. Lead is removed by adsorption on CaCO₃ from neutral or alkaline soln. The nickel complex with diethyldithiocarbamate is extracted from alkaline soln. with *iso*amyl alcohol and the absorbance measured at 325 mμ. The procedure has an absolute sensitivity of 0·0048 μg of Ni per sq. cm for an absorbance of 0·001 unit. The standard deviation for 0·5 μg of Ni is ± 4·0%.　　　　　N. E.

2709. Investigation of the Vidic method for the determination of alcohol [in blood]. W. Paulus and H. J. Mallach (Univ. Bonn, Germany). *Dtsch. Z. ges. gerichtl. Med.*, 1956, **44**, 773–780.—Oxidation of ethanol with V₂O₅ - H₂SO₄ (**I**) gave 4 mol. of VOSO₄ (**II**) for each mol. of ethanol. The absorption spectra of **I** and **II** in the visible range did not overlap, and ethanol in blood can be determined

by heating with **I** for 4 hr. at 89° and determining **II** at 570 mμ or at its max. extinction at 730 mμ. The method is not specific, as other org. compounds reduce **I** to **II**. (*Cf.* Vidic, *Anal. Abstr.*, 1955, **2**, 1276, 1277.)   CHEM. ABSTR.

2710. Semi-micro method for the determination of salicylate levels in blood. J. I. Routh, W. D. Paul, E. Arredondo and R. L. Dryer (Dept. of Biochem., State Univ. of Iowa, Iowa City, U.S.A.). *Clin. Chem.*, 1956, **2** (6), 432–438.—Add 0·2 ml of blood, serum or plasma to 0·3 ml of 6 N HCl and 0·5 ml of H$_2$O in a 12-ml glass-stoppered centrifuge tube, rinsing the pipette with the soln. several times. Add 6 ml of 1:2-dichloroethane and shake for 5 min. Centrifuge and transfer 5 ml of the 1:2-dichloroethane layer to a similar tube containing 3 ml of H$_2$O and 0·1 ml of 1% Fe(NO$_3$)$_3$ in 0·07 N HNO$_3$. Shake again for 5 min., centrifuge and measure the absorption of the water layer at 540 mμ. Read the salicylate content from a standard curve. By using a sensitive spectrophotometer with microcells it is possible to determine salicylate levels as low as 0 to 50 μg per ml. Two calibration curves are used covering the ranges 0 to 120 μg per ml and 0 to 60 mg per 100 ml. H. F. W. KIRKPATRICK

2711. A simplified method for the detection of barbiturates in toxicological materials. J. W. Huisman (Apotheek Wilhelmina Gasthuis, Amsterdam, Holland). *Pharm. Weekbl.*, 1956, **91** (14), 505–510.—Elvidge's method (*Quart. J. Pharm. Pharmacol.*, 1940, **13**, 219) has been simplified and applied to urine. The urine is acidified and extracted with CHCl$_3$ from which the barbiturate is extracted with 0·5 N NaOH. The extinction is measured between 225 mμ and 260 mμ and a curve is plotted. From the difference between the minimum at 230 to 235 mμ and the maximum at 250 to 255 mμ the presence of a barbiturate is detected. Barbitone, phenobarbitone, butobarbitone, allobarbitone, cyclobarbitone, methylphenobarbitone, heptobarbitone, amylobarbitone, aprobarbital and hexobarbitone were examined.   P. RENTENAAR

2712. Nitrofurantoin estimation in urine with the aid of chromatography. R. C. Bender, E. G. Nohle and M. F. Paul (Eaton Lab. Div., Norwich Pharmacal Co., Norwich, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (6), 420–426.—The nitrofurantoin [1-(5-nitro-2-furfurylideneamino)hydantoin] is adsorbed on to a chromatographic column, eluted and determined either by measurement of the extinction of the eluate or by formation of the phenylhydrazone and subsequent colorimetric measurement.
H. F. W. KIRKPATRICK

2713. Determination of 3:3′-dichloro- and 3-hydroxy-benzidine [in urine]. P. Engelbertz and E. Babel (Farbwerke Höchst, Germany). *Zbl. Arbeitsmed. u. Arbeitsschutz*, 1956, **6**, 58–60.—The method developed by the authors for the determination of benzidine deriv. in urine (*Ibid.*, 1953, **3**, 161) is not applicable to deriv. with electronegative substituents such as 3:3′-dichlorobenzidine (**I**). For the determination of **I**, the urine is extracted with CCl$_4$ - CHCl$_3$ and the extract is irradiated with a mercury-vapour lamp, by which HClO formed from CHCl$_3$ oxidises **I** to a quinoidal system, the green colour of which is measured. 3-Hydroxybenzidine in urine is extracted with methyl tolyl ether, acidified with acetic acid to pH 5·5, and treated with a 0·02% soln. of K 1:2-naphthaquinone-4-sulphonate; the resulting bluish-red colour is measured.   CHEM. ABSTR.

2714. A simple test for the detection of occult blood in urine. H. M. Free, A. H. Free, A. S. Giordano and C. M. Ziems (Miles-Ames Res. Lab., Elkhart, Ind., U.S.A.). *J. Urol.*, 1956, **75**, 743–752.—A reagent tablet containing *o*-tolidine is placed on a small square of filter-paper and moistened with a drop of the test urine. Water is added to the tablet and the paper is observed 2 min. later; a blue colour denotes a positive reaction. The new test minimises the variable response caused by urine antagonists to the peroxidase reaction. Good correlation of results with the chemical test on uncentrifuged urine and the results of microscopic examination of urine sediment was obtained in over 1000 urines from hospital patients and 100 urines from healthy subjects.   CHEM. ABSTR.

2715. A rapid test for occult blood in the faeces. V. P. Firth. *Guy's Hosp. Rep.*, 1955, **104**, 130–134.—The results obtained with the B.BP. test (benzidine and barium peroxide test) on 71 specimens of faeces were compared with those given by the standard benzidine, guaiacum and haematoporphyrin tests. The B.BP. test gave constant results with repeated tests on each of three specimens. Agreement with standard tests was obtained with 91% of the specimens. By the use of boiled faeces to eliminate false weak positive results the accuracy was increased to 95%.   CHEM. ABSTR.

2716. A quick and easy method of blood-sugar estimation. M. H. Davies and R. G. Paley (Dept. of Med., Univ. of Leeds, England). *Brit. Med. J.*, 1957, 501–502.—A clinical trial of a commercially developed test is described. A tablet (*A*) containing sulphosalicylic acid is dissolved in 2 ml of water in a graduated tube and 1 ml of oxalated blood is added. The liquid is mixed and filtered into another tube, collecting 1 ml of filtrate; a tablet (*B*) containing CuSO$_4$, NaOH, NaHCO$_3$ and citric acid is added, and when the soln. ceases to boil it is shaken three or four times, then allowed to stand for 30 sec., and the colour is compared with a chart provided. The results showed in general a good agreement with those of the Hagedorn - Jensen method, although an occasional grey or muddy tinge in the final colour made it difficult to read; in such instances a repeat test usually produced a satisfactory colour. The tablet test is recommended for emergency use.
H. F. W. KIRKPATRICK

2717. Rapid method for the estimation of blood sugar. R. A. Osborn (Derbyshire Royal Infirmary, Derby, England). *Brit. Med. J.*, 1957, 502–503.—The tablet test described (*cf. Anal. Abstr.*, 1957, **4**, 2716) has been tried out clinically and is recommended for emergency use.
H. F. W. KIRKPATRICK

2718. Tissue components of the domestic fowl. [Determination of] the D-glucose content of whole blood. D. J. Bell (Agric. Res. Council Poultry Res. Centre, Edinburgh). *Biochem. J.*, 1957, **66** (1), 137–141.—The stabilised benzidine reagent of Jones and Pridham (*cf. Anal. Abstr.*, 1954, **1**, 3073) is used for this colorimetric determination. On suitably prepared blood filtrates the method gives results that agree with those obtained with D-glucose oxidase.   J. N. ASHLEY

2719. A new method for the determination of inulin in plasma and urine. A. Heyrovský (Lab. of the Second Med. Clinic, Charles' Univ., Prague, Czechoslovakia). *Clin. Chim. Acta*, 1956, **1** (5),

470–474 (in English).—To 1 ml of plasma filtrate (1 in 5) or dil. urine (1 in 100) containing 0·01 to 0·1 mg of inulin add 0·2 ml of indol-3-ylacetic acid soln. (0·5% in 96% ethanol) and 8 ml of conc. HCl. Mix and allow to stand at room temp. overnight. Treat a standard soln. similarly. Prepare blanks with plasma and urine obtained before administration of inulin, and a reagent blank with 1 ml of H_2O. Read the purple - violet colour at 530 mμ. Deproteinise the plasma with $CdSO_4$ - NaOH, $ZnSO_4$ - NaOH or trichloroacetic acid. For standard soln. dilute a stock soln. containing 1 mg of inulin (a pure white prep., recryst., if necessary, from ethanol with charcoal) per ml to give 0·02 to 0·10 mg per ml.   H. F. W. KIRKPATRICK

2720. Inositol in seminal plasma [determination]. E. F. Hartree (A.R.C. Unit of Reproductive Physiol., Molteno Inst., Cambridge). *Biochem. J.*, 1957, **66** (1), 131–137.—A microbiological method, in which the yeast *Kloeckera brevis* is used, is described for the determination of free and total inositol in seminal plasma.   J. N. ASHLEY

2721. The quantitative estimation of pyruvic and α-oxoglutaric acids by paper chromatography in blood, urine and cerebrospinal fluid. B. McArdle (Med. Res. Council, Guy's Hosp. Med. Sch., London). *Biochem. J.*, 1957, **66** (1), 144–148.—A simplified method is described for the separation of 2:4-dinitrophenylhydrazones of α-keto acids by paper chromatography and for the determination of the separated hydrazones of pyruvic and α-oxoglutaric acids. The 2:4-dinitrophenylhydrazones are extracted from the paper with aq. Na_2CO_3 - NaOH and the intensity of the coloured soln. is determined. The amount of acid is ascertained from a standard graph.   J. N. ASHLEY

2722. Determination of oxalate in urine. E. R. Hausman, J. S. McAnally and G. T. Lewis (School of Med., Univ. of Miami, Coral Gables, Fla., U.S.A.). *Clin. Chem.*, 1956, **2** (6), 439–444.—Urine at pH 4·9 to 5·1 is treated with Lloyd's reagent and the oxalate in the filtrate is pptd. as the calcium salt. After being washed, the Ca oxalate is dissolved in N H_2SO_4, indole soln. is added and the mixture is made strongly acid with conc. H_2SO_4. The ppt. to red colour which develops after 45 min. at 80° to 90° is compared with standard soln. (ranging from 0·2 to 2·0 mg of oxalic acid per tube) similarly treated.   H. F. W. KIRKPATRICK

2723. Glutamine and glutaminase in blood. F. L. Iber and J. Bruton (Dept. of Metabolism, Walter Reed Army Med. Centre, Washington, D.C., U.S.A.). *Clin. Chem.*, 1956, **2** (6), 413–419.—Glutaminase is estimated by measuring the NH_3 liberated from a glutamine substrate by the Conway microdiffusion method. Glutamine is estimated by measuring the NH_3 liberated by the action of a glutaminase prep. on glutamine. The glutaminase prep. is a kidney homogenate from rats made acidotic by feeding NH_4Cl.
                H. F. W. KIRKPATRICK

2724. A method for serotonin [5-hydroxytryptamine] estimation in urine. K. Gaedtke and K. Schreier (Univ.-Kinderklinik, Heidelberg, Germany). *Clin. Chim. Acta*, 1956, **1** (5), 475–477.—Urine (100 ml) is adjusted to pH 4 with glacial acetic acid and applied to a column of 20 g of activated charcoal, contained in a glass tube, so that all of the urine passes through in about 3 hr.

The column is washed with 40 ml of H_2O and the indole and phenol bodies are then removed by washing with 200 ml of ethanol - glacial acetic acid (4:1). The charcoal is dried *in vacuo* and the 5-hydroxytryptamine (I) is acetylated by boiling with 30 ml of acetic anhydride for 1 hr.; 30 ml of 96% ethanol is added and the soln. is allowed to stand for 10 min. The charcoal is collected on a small crucible and washed (× 5) with 40 ml of ethyl acetate; the combined washings are evaporated almost to dryness, 1·5 ml of ethyl acetate is added and the ppt. is centrifuged off. The brown supernatant liquid is made up to a known vol. and an aliquot is chromatographed on Whatman No. 1 filter-paper with butanol - glacial acetic acid - H_2O (4:1:1) as solvent. The air-dried paper is sprayed with a mixture of equal parts of 10% xanthhydrol in methanol and glacial acetic acid, re-dried and exposed to HCl vapour; I shows as a greenish-blue spot. After a few min. the spot is cut out and eluted with glacial acetic acid - methanol (2:1) and the colour measured at 640 mμ. A standard curve is prepared with I - creatinine sulphate measured at 580 mμ or at 640 mμ after acetylation. The R_F of acetylated I is 0·9. Recovery of added I was 80 to 83%.
                H. F. W. KIRKPATRICK

2725. Studies in vitamin-E deficiency. III. The estimation of tissue tocopherol with molybdophosphoric acid. H. Rosenkrantz (Worcester Foundation for Exp. Biol., Shrewsbury, Mass., U.S.A.). *J. Biol. Chem.*, 1957, **224** (1), 165–174.—A sensitive, colorimetric micro-method is described in which the molybdophosphoric acid reagent of Nair and Magar (*Indian J. Med. Res.*, 1954, **42**, 557) is used. The sensitivity is increased by carrying out the determination at 100° for 2 min. and the extinction of the yellow - green colour is measured at 700 mμ. The method is specific for α-tocopherol, but owing to differences in reaction rates it will also distinguish between α-, β-, or γ-, δ-, and ζ-tocopherols. The limitations of the method, which can also be used to detect minute amounts of tocopherol and the corresponding quinols on paper chromatograms, are discussed. Fatty acids, glycerol and cholesterol do not interfere.   J. N. ASHLEY

2726. Chromatographic separation of the higher fatty acids in human blood serum. Č. Michalec (Central Lab., Univ. Hospital, Prague, Czechoslovakia). *Čas. Lék. Čes.*, 1956, **95** (5), 126–128.—Ascending chromatography is used with Whatman No. 3 paper impregnated with olive oil or liquid paraffin, and with 80% ethanol or acetic acid as the mobile phase. The detection is with $AgNO_3$.
                A. HEYROVSKÝ

2727. The determination of fatty acid esters in blood and tissue fats. K. F. Gey and H. Schön [Med. Forschungsanstalt (Biochem. Abt.) der Max-Planck-Gesellschaft, Göttingen, Germany]. *Hoppe-Seyl. Z.*, 1956, **305** (4–6), 149–157.—By treatment with hydroxylamine, carboxylic acid esters are converted into hydroxamic acids, which give a red - violet coloration with Fe^{3+}, and can, therefore, be estimated colorimetrically. The conditions of the formation of the hydroxamic acids and of the ferric complexes were studied and the reproducibility was found to be greatly improved by the use of glycine buffers, and the range of the determination was extended by carrying out the reaction in a suitable solvent mixture. Removal of aldehydes, peroxides and similar substances from

the reagents was found to be of the utmost importance. The method is satisfactory for the range 1 to 50 μE and shows an error of $\pm 3\%$.

F. POWELL

2728. The purine bases of human urine. II. Semi-quantitative estimation and isotope incorporation. B. Weissmann, P. A. Bromberg and A. B. Gutman (Dept. of Med., Mt. Sinai Hosp., New York, U.S.A.). *J. Biol. Chem.*, 1957, **224** (1), 423–434.—The purine bases are adsorbed from acidified urine on Dowex 50 and eluted with aq. NH_3. Pptn. with acid $AgNO_3$ separates the purines from creatinine and amino acids, and the resulting purine concentrate is separated by two-dimensional paper chromatography. The individual spots are then eluted and each purine is determined spectrophotometrically in the eluate. The recovery is 60 to 85%, except with 8-hydroxy-7-methylguanine, the recovery of which is much less. Duplicate determinations agree within 20%. J. N. ASHLEY

2729. Paper-chromatographic detection of galacturonic and glucuronic acids. M. Gee and R. M. McCready (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 257–258.—Aq. soln. of the uronic acids are separated by paper chromatography by using ethyl acetate - pyridine - water - acetic acid (5:5:3:1) as solvent. The mixture containing glucuronic acid is partially lactonised before chromatography. Characteristic migration rates, the hydroxamic acid - Fe^{3+} test for lactones and the specific Pb acetate test for galacturonic acid serve to identify these substances.

G. P. COOK

2730. The determination of uric acid, particularly in avian excreta. J. Tinsley and T. Z. Nowakowski (Dept. of Agric. Chem., Univ. Reading, England). *Analyst*, 1957, **82**, 110–116.—Methods for the determination of uric acid in blood, milk, urine and avian excreta are reviewed. Because of the high uric acid content of poultry excreta an accurate method for its determination is required in nutritional and manurial studies. A simple and convenient method is described, based on the isolation of the uric acid from a filtered extract by centrifugal pptn. with an ammoniacal silver - magnesium reagent (prep. described), complete removal of the supernatant liquid, extraction of the ppt. with acid LiCl soln., removal of the AgCl by centrifuging, and titration of the extract with $0.01 N$ cerium ammonium sulphate soln., with o-phenanthroline - ferrous complex as indicator. A standard uric acid soln. is treated similarly and a blank titration is made on the acid LiCl soln. The accuracy is within $\pm 2\%$ for $\simeq 1$-mg amounts. The uric acid is extracted from poultry excreta with Li_2CO_3 soln., but, as uric acid rapidly decomposes at high pH values, the soln. must be freshly prepared and analysed immediately. A. O. JONES

2731. Fluorescence test in the paper chromatography of aliphatic acids. M. Pesez and J. Ferrero (Services de Recherches Roussel-Uclaf, France). *Bull. Soc. Chim. Biol.*, 1957, **39** (1), 221–222.—The chromatogram is developed, with an alcohol (*e.g.*, butanol) saturated with NH_3 as solvent, and is then carefully dried at 30° to 40° in a current of air. Complete absence of residual NH_3 is then tested for by placing a spot of the reagent on the paper when no fluorescence in light passed through a Wood's screen indicates satisfactory removal of NH_3. The paper is then sprayed with reagent

[$ZnSO_4.7H_2O$ (0.50 g), neutral sulphate of 8-hydroxyquinoline (0.70 g) and water to 100 ml] and examined in the filtered u.v. light; the ammonium salts of the acids show a yellow - green fluorescence. H. F. W. KIRKPATRICK

2732. The separation and determination of cyclic imino acids. K. A. Piez, F. Irreverre and H. L. Wolff (Nat. Inst. of Health, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1956, **223** (2), 687–697.—Two colorimetric methods are described for use with eluate fractions from an ion-exchange column. The reagent is ninhydrin in acetic acid. When the reaction is effected at room temp. the method is suitable for the determination of hydroxyproline, *allo*hydroxyproline and proline. Heating at 100° allows determination of 5-hydroxypipecolic acid, pipecolic acid, proline and baikiain (4:5-dehydropipecolic acid). The separation of these compounds by ion exchange and paper chromatography is described. The diastereoisomers of hydroxyproline are separated by these two methods, and those of 5-hydroxypipecolic acid by paper chromatography. The methods are applied to the determination of cyclic imino acids in dates. J. N. ASHLEY

2733. The fluorimetric measurement of pyridine nucleotides. O. H. Lowry, N. R. Roberts and J. I. Kapphahn (Dept. of Pharmacol., Washington Univ. Sch. of Med., St. Louis, Mo., U.S.A.). *J. Biol. Chem.*, 1957, **224** (2), 1047–1064.—The fluorimetric method of Kaplan *et al.* (*Brit. Abstr. AII*, 1952, 277) is modified to increase its reproducibility and to allow the determination of $10^{-8} M$ di- or tri-phosphopyridine nucleotide to be made in the presence of large amounts of the corresponding reduced nucleotide. Similarly, a method with the same sensitivity is given for the determination of the reduced nucleotides in the presence of large amounts of the oxidised form. This form is destroyed in dil. alkali after which the reduced form is treated with H_2O_2 in conc. alkali. This converts it first into the oxidised form and then into the fluorescent product of Kaplan. The reduced nucleotides can also be determined by their native fluorescence. The fluorescence of reduced triphosphopyridine nucleotide only is increased threefold in the presence of Mg^{2+} in dil. alkali. The fluorescence of the reduced forms of both nucleotides is greater in org. solvents than in water.

J. N. ASHLEY

2734. The photometric estimation of creatine by the diacetyl reaction. K. Kanig (Forschungsabteilung der Psychiatrischen und Nervenklinik der Freien Univ., Berlin). *Hoppe-Seyl. Z.*, 1957, **306** (4–6), 247–259.—The diacetyl reaction for guanidino groups as carried out in alkaline soln. and intensified by means of 1-naphthol was studied in order to determine its specificity and the influence of other substances present in urine. The use of 2% NaOH soln. in place of 6% was found to give higher and steadier readings. Urea and NaCl had little effect on the reaction, but uric acid had a marked negative effect; protein, *e.g.*, serum, gave readings which increased continuously with time. An improved procedure is presented for the determination of creatine, but it is not considered that it possesses any essential advantage over indirect methods for specificity, and the apparent creatine content of urine as determined by this technique may be considerably in excess of the true value.

F. POWELL

2735. Quantitative method of lysozyme determination. T. H. Lorenz, D. R. Korst, J. F. Simpson and M. J. Musser (Wisconsin Univ. Hosp., Madison, U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (1), 145–150.—The method described is based on the decrease in turbidity when samples containing lysozyme in phosphate buffer (pH 6·2) are incubated at room temp. for 20 min. with a commercial substrate. The change in turbidity is estimated photo-electrically, and the percentage transmission at 540 mμ is related to lysozyme activity by means of a calibration graph prepared with standard lysozyme at the same time as the samples are assayed. A study is made of lysozyme concn. in nasal, oral and bronchial secretions obtained in various pathological conditions, and the significance of the results is discussed.   W. H. C. SHAW

2736. Semi-quantitative estimation of urinary free amino acids by paper chromatography. V. Jirgl (Central Lab., Univ. Hospital, Prague, Czechoslovakia). *Vnitřní Lékařství*, 1956, **2** (10), 922–927.—Urine is desalted by an electrolytic desalter, and a 20-ml portion is concentrated to dryness and dissolved in 1 ml of ethanol. One-dimensional chromatography is carried out on Whatman No. 3 paper with butanol - acetic acid. Mixtures of pure amino acids (1 to 5 mg-%) are run simultaneously, and the intensity of the spots developed with ninhydrin is compared.   A. HEYROVSKÝ

2737. Polychromatic detection of amino acids on paper chromatograms and electropherograms. J. Barrollier, J. Heilman and E. Watzke (Hauptlab. der Schering A.-G., Berlin-West). *Hoppe-Seyl. Z.*, 1956, **304** (1), 21–25.—The reaction between amino acids and isatin is improved by the addition of Zn acetate. Various colours are then given not only by different amino acids, but also by different concn. of the acid. A 1% soln. (w/v) of isatin in *iso*propyl alcohol containing 1·5% (w/v) of Zn acetate is used, with the addition of 1% (v/v) of either pyridine or glacial acetic acid. The sensitivity and stability of the colours are better with the acid reagent, but an especially rich variety of colours is obtained with the pyridine reagent. The colours can be developed by heating for 30 min. at 80° to 85°, but they are more varied if they are allowed to develop for 20 hr. at room temp. The colours are insoluble in water so that excess of reagent may be washed out leaving coloured spots on a white background. The naphthaquinonesulphonic acid reagent is also improved by the addition of Zn acetate, but this reagent is not stable and must be made up fresh before use.   F. POWELL

2738. A rapid method for detecting the transformation of phenylalanine into phenylpyruvic acid. B. Hamida and L. LeMinor (Inst. Pasteur, Centre des Salmonella, Paris). *Ann. Inst. Pasteur*, 1956, **90** (5), 671–673.—The conversion of L-phenylalanine into phenylpyruvic acid by *Bacillus proteus* has been used by Henriksen (*J. Bact.*, 1950, **60**, 225) for diagnosing this organism. The following technique reduces the time required for the test from hours to 10 min. *Reagents*—(*i*) An 18-hr. culture of the strain in question on broth agar; (*ii*) L-phenylalanine—50 mg in 10 ml of water, sterilised for 30 min. at 105° and stored at 4°; (*iii*) phosphate buffer (pH 6·8)—50 ml of 0·2 M KH_2PO_4 and 23·6 ml of 0·2 M Na_2CO_3, sterilised, and stored at 4°; (*iv*) $FeCl_3$ (26%) diluted to one-third concn. with water. *Procedure*—Make a thick suspension of the 18-hr. culture in a mixture of

four drops each of soln. (*ii*) and (*iii*) and shake for 10 min. at room temp.; the addition of one drop of soln. (*iv*) should produce an immediate intense green coloration.   D-Phenylalanine does not react in this way.   P. HAAS

2739. Oxidimetric determination of methionine. F. Jančik, F. Buben and J. Körbl (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Čeksosl. Farmac.*, 1956, **5** (9), 515–516.—Methionine (I) is dissolved in water (20 ml), and conc. HCl (3 ml) and KBr (1 g) are added. The soln. is titrated with 0·1 N or 0·01 N $KBrO_3$ with potentiometric control (platinum electrode *vs.* the S.C.E.). Similar results are obtained with 0·1 M ICl as titrant; in this case no KBr is added. The average error is 0·3%. Glycine, leucine, *iso*leucine, serine, asparagine, alanine, glutamine and phenylalanine do not interfere, but cysteine, cystine and tyrosine cause high results. The use of $KBrO_3$ rather than ICl is recommended because there is a greater change of potential at the equivalence point.   J. VOLKE

2740. The estimation of small quantities of methionine in tissues. E. Strack, W. Friedel and K. Hambsch (Physiol-chem. Inst. der Karl Marx Univ., Leipzig). *Hoppe-Seyl. Z.*, 1956, **305** (4–6), 237–247.—The estimation by means of the McCarthy - Sullivan reaction (*J. Biol. Chem.*, 1941, **141**, 871) is complicated because both homocysteine and cysteine give condensation products with formaldehyde, which also react with sodium nitroprusside. The compound formed with cysteine was not studied because the concn. of cysteine found in tissues is not usually high enough for it to cause serious interference. Homocysteine and formaldehyde probably combine in simple molecular proportions to give a heterocyclic 6-membered ring compound, which is stable in acid soln. The coloured product formed from this and sodium nitroprusside is not stable in acid soln. but that formed from methionine and sodium nitroprusside is. It is therefore possible to determine both methionine and homocysteine when they are present together. A procedure is also presented for making use of the reaction with homocysteine as a means of estimating formaldehyde.   F. POWELL

2741. The determination of histidine in blood plasma. H. Frank and H. Petersen (Univ. Kiel, Germany). *Hoppe-Seyl. Z.*, 1956, **303**, 276–281.—The diazotised chloroaniline method for the determination of histidine is not specific in cases of decompensated liver cirrhosis. Interfering compounds are removed by chromatography. Heparinised plasma (10 ml) is centrifuged with 20% trichloroacetic acid (10 ml), the excess of acid is removed by ether and the aq. soln. reduced to 1 ml. After paper chromatography (*Ibid.*, 1955, **299**, 1) the histidine stripe is eluted. The diazo reagents are added, the colour is extracted with *n*-butanol (10 ml) and determined at 436 mμ. The coloured compound must be extracted within 3 min. and the reading made within 30 min. Beer's law applies up to 50 μg; the lower limit of sensitivity is 3 to 5 μg.   CHEM. ABSTR.

2742. The oxidation of tryptamine to indol-3-ylacetaldehyde by plant amine oxidase. [Determination of indol-3-ylacetaldehyde.] A. J. Clarke and P. J. G. Mann (Rothamsted Exp. Station, Harpenden, England). *Biochem. J.*, 1957, **65** (4), 763–774.—Indol-3-ylacetaldehyde is determined by oxidation with Ag_2O to indol-3-ylacetic acid, which

is estimated spectrophotometrically at 530 mμ with Salkowski reagent (FeCl$_3$ in dil. H$_2$SO$_4$). Separately prepared Ag$_2$O gives erratic results and in the recommended procedure the Ag$_2$O is pptd. in the reaction mixture. J. N. ASHLEY

2743. A ninhydrin reaction differentiating N-terminal glycine peptides from other peptides. L. J. Saidel (Dept. of Biochem., Chicago Med. Sch., Chicago, Ill., U.S.A.). *J. Biol. Chem.*, 1957, **224** (1), 445–451.—The formation of NH$_3$ by peptides, proteins and related compounds when they are treated with ninhydrin at pH 2·5 for various periods of time is determined by Conway's micro-diffusion method. Like most free α-amino acids, many peptides and esters in which glycine occupies the N-terminal position give nearly 1 mol. of NH$_3$ per mol. of reactant in 10 min. reaction time. The application of this reaction to the determination of N-terminal glycine residues in peptides and proteins is discussed; the method has a definite, though limited, use. J. N. ASHLEY

2744. New biuret reagent for the determination of proteins in cerebrospinal fluid. H. L. Rosenthal and H. I. Cundiff (Dept. of Pathol., Rochester Gen. Hosp., Rochester, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (6), 394–400.—*Reagent*—Dissolve 1·5 g of CuSO$_4$.5H$_2$O in about 500 ml of H$_2$O, add 6·0 g of EDTA (disodium salt) and 1·0 g of KI; to the soln. add 300 ml of 2·5 N NaOH, mix well and dilute to 1 litre. This reagent is stable at room temp. when stored in polyethylene containers. *Procedure*—Place 2 ml of saline, standard albumin soln. (2·5 mg per ml) and sample in separate test-tubes, add 3 ml of reagent, mix by inversion and read the colours at 540 or 550 mμ after 20 min. against the saline blank. A standard curve is linear up to about 300 mg-% of protein. The reagent eliminates turbidities, due chiefly to Ca, and gives results comparable with those obtained by the Kjeldahl method. H. F. W. KIRKPATRICK

2745. Filter-paper electrophoresis of serum proteins. L. Peña Matías (Inst. de Biología, Andina, Peru). *Bol. Soc. Quím. Peru*, 1956, **22**, 103–118.—A buffer solution based on barbitone is employed and a potential of 300 V is applied for approx. 5 hr. The proteins are stained with bromophenol blue. For quantitative interpretation a density curve is constructed with the aid of a densitometer; the individual components are then measured planimetrically. Comparisons have been made between the electrophoretic and a chemical fractionation method on serums from adults residing at sea level and at a high altitude. L. A. O'NEILL

2746. Determination of glucoproteins and glucose by the diphenylamine reaction. L. A. Abreu, R. R. Abreu and G. G. Villela (Inst. Oswaldo Cruz, Rio de Janeiro). *Rev. Bras. Biol.*, 1956, **16** (3), 317–320.—A method is described for the determination of serum glucoproteins and blood glucose with diphenylamine (**I**) in acetic acid - HCl medium. The blue colour developed is specific for hexoses and the extinction is read at 635 mμ. *Procedure* (*a*)—Serum (1 ml), in duplicate tubes, is mixed with ethanol (95%) (5 ml), centrifuged and decanted; the ppt. is washed with ethanol (5 ml) and after centrifugation is dissolved in 0·1 N NaOH (1·0 ml) and water (0·5 ml). **I** reagent [made by dissolving **I** (10 g) in ethanol to make 100 ml, and mixing the soln. (1 vol.) with glacial acetic acid (9 vol.) and conc. HCl (10 vol.)] (3 ml) is added to one tube and,

to the other, the acid mixture (3 ml). The tubes are heated at 100° for 60 min., cooled and readings taken. (*b*) To 1 ml of tungstic acid filtrate (1 : 10) of blood, plasma or serum, water (0·5 ml) and **I** reagent (3·0 ml) are added. A blank is made with water (1·5 ml) and **I** reagent (3·0 ml).
S.C.I. ABSTR.

2747. Determination of mucoproteins in blood serum. S. Janoušek (Med. Policlinic, Charles' Univ., Prague, Czechoslovakia). *Vnitřní Lékařství*, 1956, **2** (6), 481–488.—Mucoproteins are pptd. from the sulphosalicylic acid filtrate of blood serum by tungstophosphoric acid (5% soln. in 2 N HCl). The ppt. is dissolved in water at pH 9. Mucoproteins are determined by polarography, with diphenylamine, and by photometry of the spots of mucoproteins stained with bromophenol blue on filter-paper. Different sera gave fractions of identical properties. Urinary mucoproteins gave inconsistent results. The methods agreed within ± 7%. A. HEYROVSKÝ

2748. Colorimetric determination of phosphorus in phospholipids. A. E. F. H. Meijer (Zentrallab. des Akad. Krankenhauses, Leiden, Netherlands). *Proc. Kon. Ned. Akad. Wet.*, B, 1957, **60** (1), 37–42 (in German).—Digest the soln. containing 0·01 to 0·10 mg of P with 1 ml of conc. H$_2$SO$_4$ and H$_2$O$_2$ (dropwise) until clear and colourless. Boil the digest for 10 min. to destroy excess of H$_2$O$_2$ and cool. Add 5 ml of H$_2$O and 1 drop of 5% soln. of phenol-phthalein and neutralise with 5 N NaOH; add 5 N H$_2$SO$_4$ until the colour is just discharged, then add a further 0·75 ml of the acid. Wash the soln. into a 25-ml graduated tube, add 1 ml of molybdic acid soln. (dissolve 25 g of ammonium molybdate in H$_2$O, add 25 ml of conc. H$_2$SO$_4$ and then H$_2$O to 500 ml) and 0·5 ml of a soln. containing 0·5 g of quinol and 15 g of Na$_2$S$_2$O$_5$ in 100 ml of H$_2$O. Make the vol. up to 25 ml with H$_2$O and read the extinction after 60 min. Standard soln. of P treated by this procedure showed a linear relation between extinction and concn. for the range of P mentioned above. H. F. W. KIRKPATRICK

2749. Determination of aldolase in blood serum. J. Trlifajová, J. Rampas and V. Kredba (Inst. Microbiol. Epidemiol., Hosp. Bulovka, Prague, Czechoslovakia). *Čas. Lék. Čes.*, 1956, **95** (10), 267–270.—Serum is incubated with fructose diphosphate, and triose phosphates are determined colorimetrically by means of 2 : 4-dinitrophenyl-hydrazine. Clinical experiments are discussed. A. HEYROVSKÝ

2750. Studies on glucosaminidase. N-Acetyl-β-glucosaminidase in rat kidney [determination]. D. Pugh, D. H. Leaback and P. G. Walker (Biochem. Dept., Roy. Nat. Orthopaedic Hosp., Stanmore, Middlesex, England). *Biochem. J.*, 1957, **65** (3), 464–469.—The determination described is based on that of East *et al.* (*Brit. Abstr. AIII*, 1941, 470) and is suitable for use with unfractionated tissue homogenates. The substrate used is phenyl N-acetyl-β-glucosaminide, which is hydrolysed to phenol and N-acetylglucosamine, both of which are determined by spectrophotometric methods.
J. N. ASHLEY

2751. Plasma tributyrinase (lipase) in the neonatal period. M. M. Friedman and R. L. Shriro (Lebanon Hosp., New York, U.S.A.). *Clin. Chem.*, 1956, **2** (6), 407–412.—The titrimetric method of

determining lipase in plasma is modified to an electrometric procedure that enables the estimation to be carried out on 0·1 ml of sample.

H. F. W. KIRKPATRICK

2752. Manometric assay and cofactor requirements for serine hydroxymethylase. F. M. Huennekens, Y. Hatefi and L. D. Kay (Dept. of Biochem., Univ. of Washington, Seattle, U.S.A.). *J. Biol. Chem.*, 1957, **224** (1), 435–444.—The enzyme converts serine into glycine and a C_1 unit, which is then oxidised in two stages to CO_2 and the uptake of O is measured manometrically. The system is specific for L-serine and requires added di- and triphosphopyridine nucleotide, reduced glutathione, pyridoxal phosphate and tetrahydrofolic acid as cofactors; there is a partial requirement for Mn^{2+}.

J. N. ASHLEY

2753. Determination of the sterol hydroxyl group and its application to the determination of urinary hydroxysteroids. S. H. Weinmann and M. F. Jayle (Fac. de Méd., 45 rue des Saints-Pères, Paris, France). *Bull. Soc. Chim. Biol.*, 1957, **39** (1), 65–90.—Sterol hydroxyl and phenol groups are first acetylated by reaction with acetic anhydride-pyridine (1:1) for 1 hr. in boiling H_2O or with acetyl chloride-benzene (1:1) at room temp. for 1 hr. The dried residue is treated with hydroxylamine reagent and the liberated acetylhydroxylamine is determined colorimetrically with iron reagent. The use of the method in urinary steroid analysis is discussed.   H. F. W. KIRKPATRICK

2754. The estimation of 17-hydroxycorticosteroids in urine and their importance in the diagnosis of adrenocortical function. H. Breuer and W. Nocke (Chem. Abteilung, Chirurgischen Univ.-Klinik und Poliklinik, Bonn). *Klin. Wochschr.*, 1957, **35** (4), 187–191.—17-Ketosteroids and 17-ketogenic steroids were determined by the method of Gibson and Norymberski (*Ann. Rheum. Dis.*, 1954, **13**, 59) in various endocrine states. The estimation is useful in diagnosing Cushing's syndrome, adrenogenital syndrome, and post-pubertal virilism, and in following the results of substitution therapy with cortisone and cortisol.

H. F. W. KIRKPATRICK

2755. A fluorescence method for the microanalysis of Δ^4-3-oxo steroids on paper chromatograms. P. J. Ayres, S. A. Simpson and J. F. Tait (Courtauld Inst. of Biochem., Middlesex Hosp. Med. Sch., London). *Biochem. J.*, 1957, **65** (4), 647–651.—A method is described for the determination of more than 0·2 μg of Δ^4-3-oxo steroids by measurement of their fluorescence after chromatography on paper and development by treatment with blue tetrazolium and aq. NaOH. The intensity of the fluorescence is proportional to the amount of steroid if the final spot contains < 4 μg of steroid and is < 2 cm in diameter. If four spots (two of which are standards) are used for an analysis the coeff. of variation of the determination is 6 to 10%.   J. N. ASHLEY

2756. A method for the determination of aldosterone, cortisol and corticosterone in biological extracts, particularly applied to human urine. P. J. Ayres, O. Garrod, S. A. Simpson and J. F. Tait (Courtauld Inst. of Biochem., Middlesex Hosp. Med. Sch., London). *Biochem. J.*, 1957, **65** (4), 639–646.—The determination is carried out after

continuous extraction of human urine at pH 1 by $CHCl_3$ at room temp. for 24 hr. Paper chromatography of the steroids or their acetates is effected after extensive purification by column chromatography. The final spot on the paper chromatogram is measured quant. by a fluorimeter after treatment with aq. NaOH and blue tetrazolium. The recovery of steroids throughout the method is ≃ 70%. Recovery and duplicate data suggest that the coeff. of variation for the determination of aldosterone and cortisol are 15 and 7%, respectively.

J. N. ASHLEY

2757. Determination of cortisol in human plasma by quantitative paper chromatography. P. K. Bondy, D. Abelson, J. Scheuer, T. K. L. Tseu and V. Upton (Dept. of Med., Yale Univ. Sch. of Med., New Haven, U.S.A.). *J. Biol. Chem.*, 1957, **224** (1), 47–55.—The cortisol is extracted with $CHCl_3$ and after being mixed with [4-^{14}C]cortisol it is transferred quant. to paper and the chromatogram is run for 4 hr. in toluene-75% methanol. A standard spot and the experimental area are eluted with ethanol. One portion of the eluate is taken for radioactivity determination; another is treated with 0·3 N K *tert*.-butoxide and the fluorescence is measured. The amount of cortisol is ascertained from a standard graph. A correction for incomplete recovery is applied which makes use of calculations of isotope dilution after addition of the [4-^{14}C]cortisol.   J. N. ASHLEY

See also Abstracts 2642, 2644, 2645, 2777, 2854, 2860.

Drugs

2758. Pharmaceutical-chemical analysis. I. P. Fischer and A. Bürgin (Pharmaz. Inst., Univ., Bern). *Pharm. Acta Helv.*, 1956, **31** (11), 518–542.—Organic drugs are separated into three main groups by the method of Mühlemann and Bürgin according to their distribution in the systems H_2SO_4-$CHCl_3$, tartaric acid-$CHCl_3$, and aq. NH_3-$CHCl_3$-*iso*-propyl alcohol. Individual compounds are then identified and in some cases assayed by methods which involve paper chromatography, sublimation, determination of m.p., determination of eutectic temp. with an admixed substance and microprecipitation reactions.   A. R. ROGERS

2759. Ion exchange and ion exchangers. O.-E. Schultz (Pharm. Inst., Gutenberg Str. 76, Kiel, Germany). *Dtsch. ApothZtg*, 1956, **96** (52), 1246–1248.—A brief review of published work on the pharmaceutical application of ion exchangers in preparative and analytical procedures is presented.

G. R. WHALLEY

2760. Quantitative analysis of alkaloids by ion exchange. A. Fischer. *Dtsch. ApothZtg*, 1957, **97** (2), 23–25.—The alkaloid salt (0·1 to 0·2 millimole) is dissolved in 10 ml of water (methanol for morphine) and added to a flask containing 10 to 15 g of Dowex-2 resin (previously activated by treatment with 5% NaOH soln. and washed with water until neutral to litmus). The mixture is warmed to 50°, and vigorously shaken for 3 min., when 25 ml of methanol is added and the flask is shaken again for 3 min. The soln. is filtered through a glass filter, the first 25 ml returned to the flask, and the process continued until a test portion shows the absence of anions. The resin is further washed with methanol

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$(2 \times 20$ ml) at $45°$, followed by 20 ml of a methanol - water mixture $(1:1)$, and the combined eluate is then titrated with $0.1 N$ HCl, with bromocresol green as an indicator. G. R. WHALLEY

2761. Oscillopolarographic study of some alkaloids. K. Habersberger and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (5), 264–271.—Oscillopolarographic curves of cocaine, tropacocaine, atropine, apoatropine, homatropine, pelletierine, coniine and lobeline were studied with a dropping-mercury electrode. A carbon electrode was used as a reference electrode. Semi-quantitative determination from the depth of the characteristic cut-in on the curve is possible with some of the alkaloids in soln. of alkaline hydroxides. J. VOLKE

2762. Microchemical identification of some less common alkaloids. E. G. C. Clarke (Dept. of Physiol., Royal Veterinary College, London). *J. Pharm. Pharmacol.*, 1957, **9** (3), 187–192.—Crystal and colour tests are described for the identification of 40 of the less common alkaloids (*cf. Anal. Abstr.*, 1955, **2**, 2201; 1956, **3**, 2269). Reagents additional to those previously described include soln. of NH_4SCN, disodium methylarsonate, $NaAu(CN)_4$, picrolonic acid, platinum bromide, KCN, styphnic acid and trinitrobenzoic acid. A. R. ROGERS

2763. The gravimetric assay of papaverine and strychnine with Kalignost [sodium tetraphenylboron]. O. Aklin and J. Dürst (Pharm. Inst. Eidg. Tech. Hochschule, Zürich). *Pharm. Acta Helv.*, 1956, **31** (10), 457–476.—The preparation, properties and uses of Na tetraphenylboron (**I**) are reviewed and the behaviour of 100 nitrogen-containing pharmaceutical substances towards **I** are tabulated. It is shown that careful control of conditions, especially the nature of the washing liquid and the temperature of drying, is essential for the accurate gravimetric assay of alkaloidal salts with **I**. Methods are described for the assay of papaverine hydrochloride (**II**) and of strychnine nitrate (**III**). *Procedure*—Add sufficient Na acetate soln. to a $0.002 M$ soln. of the sample (50 ml) to bring the pH to 5.0 (for **II**) or 5.5 (for **III**). Heat to $70°$ and slowly add $0.1 M$ aq. **I** reagent (1.5 ml), dropwise, with constant stirring. Cool in ice to $10°$, filter through a porcelain A2 crucible, wash the ppt. with cold 0.2% acetic acid (20 ml) and dry to constant wt. at $80°$. A. R. ROGERS

2764. Titration of apomorphine hydrochloride in a non-aqueous medium. A. Paulsen (Univ. Farm. Inst., Blindern, Oslo). *Medd. Norsk Farm. Selsk.*, 1956, **18** (9), 145–148.—Two methods have been developed. *(i)* Dissolve 0.300 g of apomorphine hydrochloride in 30 ml of glacial acetic acid by heating. Cool the soln. to $30°$ and add 10 ml of 5% mercuric acetate in glacial acetic acid followed by 20 ml of dioxan. The resulting blue soln. is titrated immediately with $0.1 N$ HClO$_4$ in glacial acetic acid until the colour changes to bright red. *(ii)* Dissolve 0.300 g of the hydrochloride in 30 ml of glacial acetic acid. Cool to between $10°$ and $15°$ and then add the other two reagents in the same quantities as before. To the resulting colourless soln. add five drops of crystal violet indicator (P. Dan. 1948 Add.) and titrate at once with $0.1 N$ HClO$_4$ until the colour changes to blue. The results of 12 experiments, expressed as the percentage of the wt. of the sample (containing 2% of water, determined by drying over H_2SO_4 to constant

wt.), gave mean values of 97.43 and 97.65%, respectively, by methods (*i*) and (*ii*), and closely similar results were obtained by potentiometric titration. P. HAAS

2765. Titration in non-aqueous media in pharmaceutical analysis. I. Semi-micro determination of ergot alkaloids. L. Šafařík and V. Bumba [Pharm. Kontrollinst. (KÚF), Prague]. *Pharm. Zentralh.*, 1957, **96** (1), 3–6.—The purity of semi-micro quantities of ergometrine maleate, and ergotamine tartrate and bitartrate may be determined by direct titration with $0.05 N$ HClO$_4$ in glacial acetic acid, with crystal violet as indicator. The proposed method is simpler and more rapid and accurate (limits of error $\pm 0.6\%$) than the official colorimetric procedures. A. R. ROGERS

2766. Complexometric titrations in pharmaceutical analysis. XV. Selective determination of quinine hydrochloride. B. Buděšínský and E. Vaníčková (Res. Inst. Pharm. Biochem., Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (5), 277–279.—Quinine hydrochloride (10 to 30 mg) dissolved in acetone - benzene $(1:1)$ (6 ml) is pptd. with a fresh $0.05 M$ soln. of CuCl in acetone. The pptd. complex, $(C_{20}H_{25}N_2O_2)_2.CuCl_2.xCH_3COCH_3$, is washed thoroughly with the solvent and dissolved in boiling water (50 ml). To the cold soln. are added six drops of aq. NH_3 (25%) and murexide as indicator; the soln. is titrated with EDTA (disodium salt) until violet - red. Cinchonine hydrochloride, quinidine sulphate, acetylsalicylic acid, phenacetin, caffeine, ephedrine hydrochloride, codeine phosphate and papaverine hydrochloride do not interfere. J. VOLKE

2767. Determination of crystalline reserpine in anhydrous medium. J. Bayer (Anal. Lab., Pharm. Factory of Kőbánya, Budapest, Hungary). *Magyar Kém. Foly.*, 1956, **62** (10), 355–356.—Dissolve reserpine (**I**) (30 to 130 mg) in water- and anhydride-free acetic acid (**II**) (25 ml) with protection from light. Add a 1% soln. of crystal violet in **II** (one drop) and titrate with $0.1 N$ HClO$_4$ in **II** to the first colour-change (violet to blue). For the determination of smaller amounts, dissolve **I** (10 to 40 mg) in water- and alcohol-free CHCl$_3$ (**III**) (50 ml), stabilised with 1% of light petroleum. Titrate 5-ml portions in the presence of a 0.1% soln. of p-dimethylaminoazobenzene in **III** (one drop) with $0.005 N$ toluene-p-sulphonic acid in **III** to a carnation-red colour. Both titrating soln. are standardised against *sym.*-diphenylguanidine. The mean deviation of a single determination is $\pm 0.3\%$ for the macro method and $\pm 0.6\%$ for the micromethod. A. G. PETO

2768. The analysis of reserpine. J. Reichelt (Pharm. Control Inst., Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (9), 516–519.—A colorimetric method for the determination of reserpine in tablets is based on the formation of an addition product of reserpine with methyl orange (molecular ratio $1:1$). *Procedure*—Pulverised tablets ($\simeq 0.5$ mg of reserpine) are shaken with 10 ml of water for 5 min., a 25% soln. of Na_2HPO_4 (10 ml) is added, and reserpine is extracted with CHCl$_3$ (4 $\times$ 25 ml). The CHCl$_3$ extract (25 ml) is mixed with 5 ml of reagent A (0.1 g of methyl orange dissolved in 100 ml of warm 4% H_3BO_3 soln.), and shaken vigorously for 3 min. To the lower layer is added anhyd. Na_2SO_4 (0.2 g), and the completely clear soln. is decanted. A portion (5 ml) is mixed with 1 ml of

reagent *B* (1 ml of conc. H_2SO_4 in 50 ml of ethanol), and the colour is measured. The concn. of reserpine is calculated from a standard curve. The presence of reserpine was detected by paper chromatography on Whatman No. 1 paper (impregnated with form-amide - ethanol, 1 : 1). The chromatogram is devel-oped with formamide - benzene. In u.v. light a greenish-blue fluorescence appears on chromato-grams dried at 120°.   J. VOLKE

2769. Alkaloids of *Rauwolfia* species. II. Estima-tion of reserpine in samples of rauwolfia by means of countercurrent distribution. D. A. A. Kidd and P. G. W. Scott (May and Baker Ltd., Dagenham, Essex). *J. Pharm. Pharmacol.*, 1957, **9** (3), 176–180.—The behaviour of reserpine (**I**) when distri-buted between various organic solvents and aq. acetic acid, and between ether - $CHCl_3$ (3 : 1) and aq. buffer soln., has been examined in a counter-current apparatus. With the latter system, the logarithm of the partition coeff. varies linearly with pH in the range 2·4 to 3·2; at pH 3·1, the partition coeff. is 1 and the partition isotherm is linear over the range of concn. 0·1 to 0·4% (w/v) of **I** in the solvent phase. This is the basis of a method for the estimation of **I** in small samples of *R. serpentina* and *R. vomitoria*. For three samples, the results showed satisfactory agreement with the yields of **I** isolated from larger quantities of the same material. *Procedure*—Extract the root with methanol and isolate a fraction which is rich in **I**. Dissolve an aliquot in $CHCl_3$ (6·25 ml) and dilute to 25 ml with ether. Clarify by centrifuging and carry out 17-transfer countercurrent extraction on a 20-ml aliquot, with $CHCl_3$ - ether (1 : 3) as mobile phase and citrate - phosphate buffer of pH 3·1 as stationary phase. Add aq. NH_3 to each tube, shake and measure the extinction at 268 mμ of aliquots of the upper phases; log ϵ for **I** at 268 mμ is 4·21. If desired, evaporate the combined upper phases to dryness and examine the purity by ascending paper chromatography and by paper electrophoresis.
                                          A. R. ROGERS

2770. Colorimetric determination of rauwolfia alkaloids in pharmaceutical preparations with am-monium reineckate. H. Wunderlich (Staatl. Inst. für Arzneimittelprüfung, Radebeul, Germany). *Pharm. Zentralh.*, 1957, **96** (2), 68–71.—The concn. of rauwolfia alkaloids in pharmaceutical prepara-tions can be determined colorimetrically as their reineckates in methanol soln. Beer's law is obeyed for concn. $< 10^{-4}$ *M*. *Procedure*—Heat an extract of the sample (containing 2 to 10 mg of alkaloid) in methanol - 15% acetic acid - water (4 : 3 : 3) (10 ml) on a bath of boiling water to remove excess of methanol, cool, and add ether (10 ml), shake, cool in ice and add 2% ammonium reineckate soln. (3 ml). After 40 min., filter through sintered glass (G4), wash the ppt. with ether (2 × 5 ml), dissolve it in methanol (10 ml) and measure the extinction at 427 mμ.   A. R. ROGERS

2771. Method of estimating the salts of the quaternary ammonium bases. II. Estimation of atropine methylbromide, atropine methylnitrate, Buscopan [hyoscine butylbromide], Decacuran [de-camethonium bromide], Doryl [carbachol], Esmodil [meprochol], Flaxedil [gallamine], Neu-Cesol, Pacyl and Succinyl [suxamethonium chloride]. J. Knabe (Inst. Pharm. und Lebensmitt. Tech. Hochschule, Brunswick, Germany). *Dtsch. ApothZtg*, 1956, **96** (52), 1243–1246.—Quaternary salts are estimated by titration, after passage of their aq. soln. through a suitable ion-exchange resin (IRA 400, Merck III). Compounds are classified into three groups. (*i*) For compounds having no ester groups, *e.g.*, meprochol, a weighed quantity of the salt is dissolved in 10 ml of water and passed through a resin column at a rate of 1 ml per min., the column is finally washed with water (4 × 10 ml), and the eluate titrated with 0·1 *N* HCl, with Tashiro indicator. The titration soln. is boiled to expel CO_2, and titrated to a green end-point. (*ii*) Compounds with an ester group present, *e.g.*, atropine methylbromide, are treated as in method (*i*), 10 ml of 0·1 *N* HCl and 10 ml of water are added to the eluate, and the excess of acid is back-titrated with 0·1 *N* NaOH soln. (*iii*) Compounds in which an ester group is present and obtained by saponifying a base having a betaine structure, *e.g.*, Neu-Cesol, are dissolved in 10 ml of methanol and passed through a resin column, previously treated with 4% NaOH soln., and washed first with water and finally with methanol (3 × 10 ml). The column is washed with methanol and the eluate treated as under (*ii*).
                                        G. R. WHALLEY

2772. Determination of tetracyclines. A. Fouchet (École de Méd. et Pharm., Angers, France). *Ann. Pharm. Franç.*, 1956, **14** (7–8), 553–555.—The colour reaction (*cf. Anal. Abstr.*, 1957, **4**, 1329) given by tetracycline, chlortetracycline and oxy-tetracycline with conc. aq. $ZnCl_2$ was investigated and is applied to the determination of the pure compounds.   E. J. H. BIRCH

2773. Simultaneous determination of chlortetra-cycline and tetracycline. J. Doskočil (Res. Inst. for Antibiotics, Roztoky, Czechoslovakia). *Československ. Farmac.*, 1956, **5** (6), 321–323.—The colorimetric determination of chlortetracycline (**I**) and tetra-cycline (**II**) is based on the different rates of inactiva-tion of **I** and **II** in 0·2 *M* Na_3PO_4. *Procedure*—The dissolved sample (1 ml containing 1 mg) is mixed in two flasks with 0·2 *M* Na_3PO_4 (10 ml) and 0·2 *M* phosphate buffer pH 6 (10 ml), respectively. After 30 min., 2 ml of each soln. is mixed with 2*N* HCl (5 ml) and heated in a boiling-water bath for 5 min. Water (5 ml) is added to the cooled soln. and extinctions are read at 440 mμ. The same procedures are made with standard samples of **I** and **II**. The concn. in the mixture are given by the following equations—

$$C_T = \frac{E_a - b.E_k}{k_T\,(a - b)} \text{ for } \mathbf{II},$$

$$C_C = \frac{a.E_k - E_a}{k_C\,(a - b)} \text{ for } \mathbf{I},$$

where C_T and C_C are concn. of **II** and **I** in the sample, respectively, k_T and k_C are extinction coefficients (after heating with 2 *N* HCl) for the concn. 1 mg per 1 ml, E_k and E_a are extinctions of the sample obtained from buffer pH 6 and from Na_3PO_4, respectively; the values *a* and *b* correspond to the ratio of the extinction coefficient after alkaline inactivation to the normal extinction coefficient—

$$a = \frac{k_{Ta}}{k_T}, b = \frac{kC_a}{k_C}. $$ The average error is 2·5% from the sum for **I**, and 5% for **II**. The method has been used for the analysis of fermentation broth.
                                          J. VOLKE

2774. Miamycin, a new antibiotic. H. Schmitz, M. Risiek, B. Heinemann, J. Lein and I. R. Hooper (Bristol Lab. Inc., Syracuse, N.Y., U.S.A.). *Anti-biot. & Chemother.*, 1957, **7** (1), 37–39.—Descriptions

are included of the physical properties and chemical reactions of miamycin, a new antibiotic of the erythromycin group obtained by growth of an organism closely related to *Streptomyces ambofaciens* in a suitable medium. Information is given on optical rotation, i.r. and u.v. absorption curves, colour and pptn. reactions, on paper chromatography, and on minimum inhibitory concn. for various organisms. W. H. C. SHAW

2775. Cobalamin assay by the radio-isotope tracer method. A collaborative study report of the U.S.P. - N.F. joint panel. C. F. Bruening, J. D. Neuss, P. Numerof and O. L. Kline (Div. of Nutrition, Food and Drug Admin., Washington, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (1), 66–72.—Four commercial-type samples were examined by the radio-isotope tracer method of the first supplement to the U.S.P. XV, and the method was found to be specific for cobalamins. Biologically inactive "red pigments" which might occur in commercial products do not interfere. For those samples that did not contain "red pigments" the results were in good agreement with those of the U.S.P. microbiological method. A. R. ROGERS

2776. Estimation of vitamin B₁₂ᵦ (hydroxocobalamin) in proteolysed liver extracts. V. Sreenivasamurthy, M. Swaminathan and V. Subrahmanyan (Central Food Technol. Res. Inst., Mysore). *J. Sci. Ind. Res., India, C*, 1956, **15** (10), 215–217.—The effect of various concn. of Fe on the destruction of hydroxocobalamin (I) in proteolysed liver extracts by ascorbic acid - Na ascorbate (II) was investigated. It was found that, at a concn. of 50 μg per ml of extract, Fe gave complete protection against II, but when the extract was diluted to reduce the Fe to about 1 μg per ml, I was completely destroyed by II. Conversion of I into cyanocobalamin before treatment with II resulted in negligible loss of potency. Based on these results, a method has been developed for the estimation of I. O. M. WHITTON

2777. Determination of methionine in pharmaceutical preparations. B. Gauthier and L. Le Dreff. *Ann. Pharm. Franç.*, 1956, **14** (7–8), 532–537.—Methods for the determination are reviewed, and the direct titration of the –SH group by oxidation with bromide - bromate soln. to disulphide is described. *Procedure*—Prepare the standard by dissolving samples of 0·1 to 0·15 g of methionine, or corresponding amounts of its derivatives, in 10 ml of water and 25 ml of glacial acetic acid, and titrate with 0·1 N bromide - bromate to a faint yellow endpoint. Prepare and titrate similar soln. from pharmaceutical preparations. (29 references). E. J. H. BIRCH

2778. The decomposition of acetylsalicylic acid in some commercial preparations. B. S. Goei The and Tjoa Kian Kie (Pharmaceut. Lab., Univ. Indonesia, Bandung). *Pharm. Weekbl.*, 1956, **91** (14), 501–503.—It was found that commercial tablets containing acetylsalicylic acid, whether or not combined with other medicines, were often decomposed. The determination of salicylic acid is based on the colour reaction with Fe^{3+}, the sensitivity of which is 1 in 8×10^5. The extinction is measured at 530 mμ. A blank determination is also made. P. RENTENAAR

2779. Rapid method for the determination of phenacetin in the presence of acetylsalicylic acid, caffeine and codeine. O. Falex (Tromax Pty. Ltd., Melbourne). *Australasian J. Pharm.*, 1956, **37**, 7–8.—A simple method for determining phenacetin consists in hydrolysis with 10% (w/w) H_2SO_4 and titration of the p-phenetidine formed with $NaNO_2$. CHEM. ABSTR.

2780. Determination of sympathomimetic amines by ion exchange. M. C. Vincent, E. Krupski and L. Fischer (College of Pharmacy, Univ. of Washington, Seattle). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (2), 85–87.—The recovery of sympathomimetic amines from soln. of their salts by means of three ion-exchange resins has been studied. Amberlite IRA-400 is not suitable for the amines possessing phenolic groups. Amberlite IRC-50 is not suitable with preparations containing Na^+ or similar interfering cations. Amberlite IR-45, a weakly basic anion-exchange resin, is recommended for the assay of sympathomimetic amines (including those containing phenolic groups) and their preparations which do not contain local anaesthetics or antihistamines; Na^+ do not interfere. If the resin columns are properly buffered, and wrapped with aluminium foil, the method can be applied to those amines that are easily decomposed by alkali or light. Modifications of the procedure previously described (Vincent *et al.*, *J. Amer. Pharm. Ass., Sci. Ed.*, 1953, **42**, 754) are given for the assay of elixirs, syrups, capsules, tablets, jellies, suspensions, inhalants, emulsions and oily soln. A. R. ROGERS

2781. Acidimetric determination of hexamine with potentiometric indication. G. Dušinský (State Inst. Control of Drugs, Bratislava, Czechoslovakia). *Československ. Farmac.*, 1956, **5** (5), 274–275.—Hexamine (I) (0·1 to 0·5 g) in H_2O (25 ml) or in 50% acetone is titrated with 0·1 N or 0·5 N HCl, with an antimony indicator electrode. Small amounts of NH_3 may be determined simultaneously. The dissociation constant of I was determined as $K_b = 8 \times 10^{-10}$; the potential of the antimony electrode at the equiv. point is approx. $-0·14$ V to $-0·17$ V *vs.* the S.C.E. The relative error is $\simeq 1\%$. J. VOLKE

2782. Determination of sulphonamides in tablets. M. Béguin (Lab. Pharm. Galén., Univ. Geneva). *Pharm. Acta Helv.*, 1957, **32** (1), 13–34 (in French).—The argentimetric method of determining sulphonamides has been applied to tablets of sulphadimidine, sulphathiazole and phthalylsulphathiazole. Of the excipients commonly used, only stearic acid and its soluble salts are likely to interfere; these can be removed by extraction methods (although emulsification may cause difficulty) or better by pptn. with Ba^{2+}. *Procedure*—To the powdered sample (containing $\simeq 1$ g of sulphonamide) add aq. NH_3 (10 ml) and water (40 ml) and a hot soln. of $Ba(NO_3)_2$ (10 g in 45 ml of water). Cool, dilute to 100 ml and mix well. To a 25-ml aliquot of the suspension add 0·1 N $AgNO_3$ (15 ml) and water (25 ml). Complete the assay according to the method of the second supplement of Pharm. Helv. V. The error is 0 to $+ 0·3\%$. A. R. ROGERS

2783. The photocolorimetric determination of sulphanilamide, sodium sulphacetamide and procaine. N. I. Krikova. *Med. Prom., SSSR*, 1956, (2), 41–44; *Ref. Zhur., Khim.*, 1956, Abstr. No.

72,075.—Photocolorimetric methods have been evolved for the determination of sulphanilamide (**I**), sodium sulphacetamide (**II**) and procaine (**III**) on the basis of an azo reaction with 8-hydroxyquinoline sulphate (**IV**). To a 0·05% soln. of **I** (0·02 to 0·07 ml) or **II** (0·05 to 0·09 ml) add 0·1 N HCl (0·25 ml) and 0·001 M $NaNO_2$ (0·5 ml), shake for 2 min., add a soln. of **IV** (0·05%) (0·3 ml) and 0·1 N NaOH (0·5 ml) and dilute to 10 ml. After mixing, transfer the coloured soln. to a photocolorimeter cell. To determine **III**, to a 0·05% soln. (0·07 to 0·13 ml) add 0·1 N HCl (0·25 ml), and 0·001 M $NaNO_2$ (0·5 ml), shake for 30 sec., add the soln. of **IV** (0·05%) (0·1 ml), dilute to 7 or 8 ml, add 0·1 N NaOH (1 ml) and dilute to 10 ml. The accuracy of the determinations is within ±5%.

C. D. KOPKIN

2784. Polarographic determination of bismuth 8-hydroxy-7-iodoquinoline-5-sulphonate (Bi-Yellon). B. Kakáč and Z. Roubal (Res. Inst. Pharm. Biochem., Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (5), 271–273.—8-Hydroxy-7-iodoquinoline-5-sulphonic acid and Bi can be determined simultaneously in McIlvaine's buffer (pH 5) containing tartrate. *Procedure*—The sample (≃ 150 mg) is dissolved in 2·5 ml of 40% Na K tartrate soln. (pH 9) and 4·0 ml of 0·1 N NaOH. The final vol. is adjusted with water to 25 ml. A 1-ml aliquot is mixed with buffer soln. (5 ml), water (4 ml) and five drops of 0·5% gelatin soln. The polarographic curves are recorded after de-aeration, and the heights of the waves of Bi and of the acid are compared with a calibration curve.

J. VOLKE

2785. Colorimetry of isonicotinic acid hydrazide [isoniazid] with *p*-dimethylaminobenzaldehyde. G. Machek (Forschungslab. der Biochemie, G.m.b.H., Kundl, Tirol). *Sci. Pharm.*, 1956, **24** (1), 11–17.—The colorimetric determination of isoniazid with a *p*-dimethylaminobenzaldehyde (**I**) reagent has been critically examined. The intensity of colour slowly reaches a max. after hydrolysis of the isoniazid for many hours in the presence of **I**. The use of a stabilised reagent, which contains **I** (400 mg), 10% aq. HCl (2 ml) and 0·5% aq. $NaNO_2$ (1 ml) in methanol (100 ml), is preferred. The method has been applied to the determination of isoniazid in tablets. *Procedure*—Extract the powdered sample by shaking with warm methanol (50 ml) for 20 min. Filter and dilute to 100 ml. Dilute a 5-ml aliquot with methanol (30 ml) and mix 5 ml of this soln. with **I** reagent (5 ml). Allow to stand at 20° for 20 min. and determine the extinction at 525 mμ.

A. R. ROGERS

2786. Polarographic determination of phenolphthalein in pharmaceuticals with glacial acetic acid as solvent. G. Dušínová and Z. Gruntová (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (6), 340–343.—In 12·5% acetic acid and 0·75 M Na acetate the height of the wave of phenolphthalein (**I**) ($E_{\frac{1}{2}} = -0·69$ V *vs.* the S.C.E.) is linearly proportional to concn. in the range 10^{-4} to $7·5 \times 10^{-4}$ M. *Procedure*—Finely powdered tablets (≃ 50 mg of **I**) are dissolved in 10 ml of glacial acetic acid and filtered into a 25-ml volumetric flask. The dissolution is repeated with 10-ml and 5-ml portions of acetic acid. A vol. corresponding to approx. 1 to 5 mg of **I** is adjusted with glacial acetic acid to 2·5 ml, and 5 M Na acetate (3 ml) and water are added to a final vol. of 20 ml. After de-aeration, the polarographic curve

is recorded. When determining **I** in liquid paraffin emulsions, the acetic acid soln. is extracted with light petroleum before recording. The soln. of tablets containing chocolate is centrifuged and extracted with light petroleum before analysis. Standard curves are used for evaluation.

J. VOLKE

2787. Polarographic determination of phenolphthalein in certain pharmaceuticals produced in Czechoslovakia. J. Blažek and Z. Stejskal (State Inst. for Control of Drugs, Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (6), 344–345.—Phenolphthalein (**I**) is extracted with 96% ethanol and the soln. is diluted with water to an ethanol concn. of 25%. For polarography, the soln. is made acid (3·8 N HCl). The evaluation is carried out by means of a calibration curve. **I** is extracted from liquid paraffin-containing emulsions with ethanol; the determination of **I** in chocolate tablets is not possible.

J. VOLKE

2788. Spectrophotometric method for estimation of menadione [menaphthone]. Vanamala Sathe, J. B. Dave and C. V. Ramakrishnan (M. S. Univ. of Baroda, India). *Anal. Chem.*, 1957, **29** (1), 155–156.—An improvement on the method of Reddy and Srinivasan (*Current Sci.*, 1948, **17**, 22) is described, which makes it possible to estimate micro quantities (2 to 300 μg) of menaphthone with the Beckman spectrophotometer.

L. S. ADLER

2789. Identification and assay of pentapyrrolidium [pentolinium] tartrate. R. Okken (Poviet Produkten N.V., Amsterdam, Holland). *Pharm. Weekbl.*, 1956, **91** (14), 503–505.—A method is described for the identification and determination of pentolinium tartrate $[C_{15}H_{32}N_2 \cdot 2C_4H_5O_6]$ (**I**). Identification tests are: (*i*) m.p. about 200° (decomp.), (*ii*) picric acid forms a ppt. which melts at 270° (decomp.), (*iii*) the reineckate ppt. decomposes at 275° to 280°. *Procedure*—Dissolve about 100 mg in 20 ml of N H_2SO_4. Heat the mixture to boiling-point and add slowly 1% ammonium reineckate soln. (30 ml) previously warmed to 40°. Allow to stand at 20° for 15 min. and for 2 to 3 hr. in an icebox. Filter off the ppt., wash with 0·004% ammonium reineckate soln. until free from sulphate, then with ethanol and ether. Dry at 80° to constant weight. Each 100 mg of residue is equivalent to 61·4 mg of **I**.

P. RENTENAAR

2790. Direct volumetric determination of elementary sulphur in pharmaceutical preparations. Z. Gruntová and G. Dušinský (State Inst. Control of Drugs, Bratislava, Czechoslovakia) *Českosl. Farmac.*, 1956, **5** (5), 275–277.—Sulphur is titrated with NaCN soln. The equivalence point is indicated either with bromocresol purple or potentiometrically. Various pharmaceutical preparations (tablets, powders, ointments) were analysed by this method. *Procedure*—A sample (≃ 10 mg of S) is dissolved in CS_2 (1 ml) and warm acetone (20 ml). Insoluble substances are filtered off, and H_2O (4 ml) is added to the filtrate. The volumetric soln. contains 0·05 M NaCN, and is prepared by dissolving NaCN (1 to 2 g) in H_2O (100 ml) and adding *iso*propyl alcohol to make up the vol. to 500 ml. After 24 hr. this soln. is filtered and its factor determined. The titration is carried out with hot soln. and with six drops of the indicator (0·1% in ethanol). The colour changes from

yellow - green to blue - violet. Santonin, H_3BO_3, $BiNO_3(OH)_2$, CS_2, CCl_4, $CHCl_3$ and ether do not interfere. The average error is $\simeq 1.5\%$.

J. VOLKE

2791. Determination of aminomercuric chloride [ammoniated mercury] with 0·1 N potassium bromate solution. D. Köszegi and M. Tornyos [Pharm.-Chem. Inst., Medizin. Univ., Szeged (Ungarn)]. *Pharm. Zentralh.*, 1957, **96** (2), 59–63.— The method of Köszegi and Salgó (*cf. Anal. Abstr.*, 1955, **2**, 593), in which hypobromite is used for the determination of NH_3, is applied to the assay of ammoniated mercury. The results show good agreement (range of error -0.10 to $+0.17\%$ for 14 samples) with those obtained by gravimetric assay. Of the other methods available, that of Kolthoff (*Pharm. Weekbl.*, 1918, **55**, 208) is preferred to those that depend on titration of the alkali liberated by the action of KI or $Na_2S_2O_3$. *Procedure*—Add 0·1 N $KBrO_3$ (40 ml) and KBr (1·5 g) to the sample (0·16 to 0·18 g) contained in a 250-ml bromination flask. Add 2 N HCl (10 ml) and allow the sample to dissolve during 5 or 10 min. Add 2 N NaOH (16 ml), shake well and allow to stand in the dark for 20 min. Add KI (1·5 g) and 2 N HCl (20 ml), set aside for 5 min., add $NaHCO_3$ (0·5 g) and titrate with 0·1 N $Na_2S_2O_3$, with starch as indicator.

A. R. ROGERS

2792. Rapid method for the determination of ethanol in tinctures and spirits. R. Fischer and W. Mühlberger (Univ. Graz, Austria). *Sci. Pharm.*, 1956, **24** (1), 17–24.—The method of Fischer and Kolmayr (*cf. Anal. Abstr.*, 1954, **1**, 2218) for the determination of ethanol in tinctures and other alcoholic soln. has been extended. The error is within 2% but is greater with samples that contain $> 3\%$ of a volatile oil.

A. R. ROGERS

2793. Volumetric micro-determination of cyanides in bitter almond water. J. Doležal, V. Simon and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Českosl. Farmac.*, 1956, **5** (6), 339–340.—When cyanides are titrated with $NiSO_4$ in ammoniacal medium, a stable complex is formed. *Procedure*—Bitter almond water (1 to 5 ml) is diluted with H_2O to 25 ml. Conc. aq. NH_3 (1 ml) is added and enough murexide indicator to give a red - violet soln. The soln. is titrated with $NiSO_4$ until yellow. The method is more sensitive than the usual titration of cyanides. J. VOLKE

See also Abstracts 2531, 2632, 2636, 2660, 2662, 2711, 2712, 2799, 2810.

Food

2794. Polarographic determination of tin in foods. J. Markland and F. C. Shenton (County Analyst's Dept., Shire Hall, Durham, England). *Analyst*, 1957, **82**, 43–45.—The whole of the contents of the can of food is thoroughly mixed, preferably in a macerator, a known weight of water being added if necessary. The sample (5 g) is wet-ashed with HNO_3 and H_2SO_4 and fumed twice with H_2SO_4 in the presence of ammonium oxalate. The residue is transferred to a 50-ml flask by rinsing with the supporting electrolyte (53·5 g of NH_4Cl dissolved in water, mixed with 89 ml of conc. HCl and diluted to 1 litre), 1 ml of a 1% (w/v) gelatin soln. is added and the vol. is adjusted at 20° with the

supporting electrolyte. The liquid in the polaro-graphic cell is de-aerated with N and the polaro-gram is recorded at -0.3 to -0.8 V, full com-pensation current being used. Under these con-ditions Sn has a half-wave potential of $\simeq -0.5$ V against the mercury-pool anode. Lead gives a wave indistinguishable from that of Sn, but Zn, Cu, Mn and Fe do not interfere. Interference by Pb is of no importance since the amount of Pb that is significant for rejection of the sample is much less than that for Sn. Recovery expt. with 1-mg amounts of Sn indicate an accuracy within $\pm 3\%$. Preliminary trials of the analysis of hexaphenyldi-tin and triphenyltin bromide gave satisfactory results.

A. O. JONES

2795. Sodium versenate [EDTA, disodium salt] for eliminating lead error in pol determinations. K. S. G. Doss and —— Vishnu. *Sugar*, 1956, **51** (11), 34, 51.—Lead forms a stable sol. complex with EDTA (disodium salt) (I). Results of analysis of fructose soln. show that the polarisation of 10 to 20 ml of the original pure soln. is almost fully restored when Pb subacetate clarification is followed by addition of 11 or 22 ml of 10% I. Since the addition lowers the pH considerably (to 3·9) a 1:1 mixture of I and NaOH is preferably used.

SUGAR IND. ABSTR.

2796. The determination of grade strength of pectins by the Teepol-gel procedure. M. Olliver, P. Wade and K. P. Dent (Chivers & Sons Ltd., Histon, Cambridge, England). *Analyst*, 1957, **82**, 127–128.—A provisional standard method for the determination of grade strength of pectins des-cribed by a Sub-Committee of the British Food Manufacturing Industries Research Association (*Analyst*, 1951, **79**, 536) has been critically examined and inconsistencies have been found that can be overcome by suitable modification (Olliver *et al.*, *J. Sci. Food Agric.*, 1957, **8**, 188). In this modified procedure the pectin soln. is mixed with a deter-mined amount of Teepol (or other suitable surface-active agent) before being boiled with sugar and acid to produce a gel of sol. solids content of 70·5 $\pm 0.5\%$ (by refractometer) and a pH value of 3.10 ± 0.05. The gel strength is then measured by the Ridgelimeter (*cf.* Cox *et al.*, *Brit. Abstr. C,* 1944, 133).

A. O. JONES

2797. Determination of mineral matter and admixed calcium carbonate in flour. Y. Pomeranz (Food Testing Lab., Haifa, Israel). *Chemist Analyst*, 1957, **46** (1), 2–3.—An aliquot of a filtered aq. extract of the ashed flour is passed through a column (10 cm × 1 cm) of Amberlite IR-120 (H form) at the rate of 1 ml per min. The column is eluted with water and the eluate is titrated with aq. NaOH; the percentage of mineral matter is calculated from a linear calibration curve of ash ($\ngeq 6\%$) *vs.* acidity released on the resin. The column is then eluted with 5 N HNO_3, the eluate and washings are adjusted to pH 12, and the Ca is titrated with 0·018 M EDTA (disodium salt), with murexide indicator. There is no interference from PO_4^{3-}.

W. J. BAKER

2798. Peroxidase-type reaction of wheaten flour. Sensitivity to rate of extraction and to treatment with chlorine dioxide. E. E. McDermott and J. Pace (Res. Ass. of British Flour Millers, Cereals Res. Sta., St. Albans, Herts., England). *Chem. & Ind.*,

1957, **(8)**, 234–235.—The colour developed in the peroxidase reaction given by wheaten flour with H_2O_2 and benzidine is less intense when the flour has been treated with ClO_2. Extracts of treated flour give the same result. A colorimetric method for studying the reaction is described, and typical results are given. No diminution of colour was found with flour that had been treated with agene, or with benzoyl peroxide. Values were sensitive to the rate of extraction of the flour. Small amounts of added germ also affected the sensitivity.

W. J. WRIGHT

2799. **Determination of ionic copper present in commercially available copper chlorophyllins.** B. M. Blank and K. Morgareidge (Food Research Lab., Inc., Long Island City, New York, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (1), 73–74.— Dissolve the sample ($\simeq 1$ g) by stirring in H_2O (75 ml). Add N HCl slowly with continuous vigorous stirring until a pH of 3·0 is reached (meter), taking care not to overshoot. Continue to stir for 10 min. Dilute to 100 ml with H_2O, mix and filter. Determine the copper content of an aliquot of the filtrate by the A.O.A.C. "carbamate" method or by use of dithizone. A. R. ROGERS

2800. **The use of differential curves in the dilatometry of fats.** H. Jasperson and A. A. McKerrigan (J. Bibby and Sons, Ltd., King Edward Street, Liverpool). *J. Sci. Food Agric.*, 1957, **8** (1), 46–54.—Differential dilatometric curves, in which the rate of expansion is plotted against temp., give much information about phase relationships of fats and provide a means of distinguishing between the melting properties of various fats and fat blends. Characteristic curves are given for simple fats, hydrogenated fats and fat blends. These curves are discussed in relation to the predominant glycerides present. H. B. HEATH

2801. **Paper-chromatographic determination of metal traces in edible fats.** K. Täufel and K. Romminger (Humboldt Univ., Berlin). *Fette, Seif., Anstrichmitt.*, 1956, **58**, 104–112.—The qual. and semi-quant. paper-chromatographic method will indicate as little as 0·1 p.p.m. of Fe, 0·05 p.p.m. of Cu or Mn, and 0·02 p.p.m. of Ni. The fat is dried, ignited at 340° and the ash dissolved in 0·5 ml of 6 N HCl. After evaporation, the residue is dissolved in 0·06 ml of 6 N HCl. A sample is pipetted on to a paper strip (S. & S. 598G) (3 cm × 22 cm), which is impregnated with 6 N HCl - butanol (1:1). The strip is developed with the solvent, and the spots are detected by means of thiocyanate for Fe, formaldoxime for Mn, and dithio-oxamide for Cu and Ni. CHEM. ABSTR.

2802. **Methods for the use of microscopic procedures in the study of chocolate.** E. Hanssen (H. Balsens Keksfabrik KG, Hanover). *Fette, Seif., Anstrichmitt.*, 1956, **58** (10), 849–852.—Chocolate or chocolate coatings can be cut with an ordinary microtome, to give sections 2·5 μ thick, without preparation. The section is transferred to a slide with a dissecting needle and fixed by allowing a drop of 96% ethanol to run over it; the ethanol dissolves some sugar and fat, but the chocolate structure is not materially altered. The sugar and fat constituents are observed in polarised light, or the fat is stained with Sudan III. With Fast green as a stain, roller-dried

and spray-dried milk aggregates, crumb milk and condensed milk can be distinguished. Adulteration of cocoa products with cocoa shells is indicated by the presence of characteristic plant tissues, the most specific being the mucilage cells. For the differentiation of these cells from roller-milk powder, meal or starch, a stain containing 2 ml of a 1% aniline blue soln. and 0·7 ml of "Skribtol" Indian ink and 10 ml of water is used. E. HAYES

2803. **Detection of rape oil in olive oil and the quantitative paper chromatography of rape oil.** H. P. Kaufmann, T. Lüssling and A. Karabatur (Inst. für Pharm. u. Lebensmittelchemie, Univ., Münster, Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (11), 985–991.—When erucic acid, which is present in large amounts in rape oil, is oxidised with alkaline $KMnO_4$ under controlled conditions, it is converted into dihydroxybehenic acid, which can be recovered quant. from the reaction mixture. On oxidation at 20° for 60 min. with a 100% excess of $KMnO_4$, mixtures of fatty acids derived from blends of rape oil with olive oil, arachis oil, maize oil or linseed oil give only insignificant amounts of acids other than dihydroxybehenic, and the presence of more than 10% of rape oil in these oils can be detected by the oxidation method. This method is superior to the modified "erucic acid number" method of Hadorn and Jungkunz (*Anal. Abstr.*, 1954, **1**, 1685). Adulteration of olive oil with more than 5% of rape oil can be detected by paper chromatography of the fatty acids by the method of Kaufmann and Nitsch (*Fette, Seif., Anstrichmitt.*, 1956, **58**, 492). As little as 1% of rape oil can be detected if the paper chromatography of the fatty acid mixture is preceded by chromatography on a column of silica gel, with nitromethane as stationary phase and light petroleum (boiling range 30° to 40°), saturated with nitromethane, as mobile phase. E. HAYES

2804. **Paper-chromatographic studies on fatty acids.** M. Jáky (Ölabteilung des Forschungsinst. für Pflanzliche Öle und Chem. Haushaltungsartikel, Budapest). *Fette, Seif., Anstrichmitt.*, 1956, **58** (9), 721–724.—The method of Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557) is applied to the separation of fatty acids of the same chain length but differing in their degree of unsaturation. Paraffin (boiling range 190° to 220°) on S. & S. paper No. 2043b, or 62, is used as the stationary phase and acetic acid (67 to 77%) as the mobile phase. Stearic, palmitic, oleic, linoleic and linolenic acids are separated from mixtures, but palmitic acid is difficult to separate from oleic unless the proportion of palmitic acid in the mixture is low. The R_F values of different fatty acids vary according to the source of the mixture being chromatographed: an adulterated oil can be identified by comparing the chromatogram of its fatty acids with that of the mixture of acids from an authentic specimen. The method can be used for the quant. determination of fatty acids, the spots being evaluated planimetrically. E. HAYES

2805. **Paper chromatography in the fat field. XIX. Quantitative paper-chromatographic determination of straight-chain fatty acids and their mixtures.** H. P. Kaufmann (Inst. für Pharm. und Lebensmittelchemie, Univ., Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (7), 492–498.— Qual. and quant. methods are reviewed, with

special reference to the work carried out since 1948. In the analysis of fatty-acid mixtures obtained from poppyseed, cottonseed and maize oils, paper chromatography gives results agreeing with those obtained by classical methods.   E. HAYES

2806. Quantitative photometric evaluation of long-chain carboxylic acids separated by paper chromatography. A. Seher (Dtsch. Inst. für Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (7), 498–504.—Long-chain carboxylic acids separated on paper chromatograms are evaluated by a photometric method. A paper chromatogram prepared by the method of Kaufmann and Nitsch (*Anal. Abstr.*, 1955, **2**, 2557) is dried and treated for 30 min. with a dil. soln. of Cu acetate. The excess of Cu is removed by washing for 1 hr. in running tap water, the chromatogram is immersed for 30 min. in a 1·2% soln. of $K_4Fe(CN)_6$ and then re-washed for 30 min. and dried. The strips are placed in a specially constructed photoelectric photometer in which light, filtered through Schott u. Gen. BG 21 (1 mm) and UG 9 (1·5 mm) filters, emerges from a 1-mm slit and passes through the paper, stretched horizontally between two glass plates and so arranged that it can be moved transversely. Absorption values are plotted against the distance of the paper strip from the starting point; the area under the curve obtained for each spot multiplied by the mol. wt. of the fatty acid represented by the spot is proportional to the amount of that acid in the mixture. With linseed, arachis, poppyseed and cottonseed oils, the method gives results agreeing with those obtained by chemical or spectrophotometric methods.   E. HAYES

2807. Paper-chromatographic detection of antioxidants. II. K. F. Gander (Margarine Union A.-G., Hamburg). *Fette, Seif., Anstrichmitt.*, 1956, **58** (7), 506.—The chromatographic method for the detection of antioxidants in fats (*Anal. Abstr.*, 1956, **3**, 562) does not give proof that antioxidants have been added to lard, shortening or margarine. Natural oils contain antioxidants and these sometimes have R_F values, and give colour reactions, similar to those of added antioxidants.   E. HAYES

2808. The determination of vitamin D and related compounds. I. Introduction and preparation of compounds in the irradiation series. W. H. C. Shaw, J. P. Jefferies and T. E. Holt (Glaxo Lab. Ltd., Greenford, Middx., England). *Analyst*, 1957, **82**, 2–7.—Physical and chemical methods for the determination of vitamins of the D group are reviewed, particularly those suitable for determining the composition of the complex mixtures formed during the irradiation of the provitamins D, *viz*, ergosterol and 7-dehydrocholesterol. The preparation, mainly by chromatography, of purified precalciferol$_2$, precalciferol$_3$, lumisterol$_2$, tachysterol$_2$, and other compounds closely related to the vitamins D is described. The extinctions of these compounds at specified wavelengths and their colour reactions with $SbCl_3$ are recorded.
II. Analysis of irradiation products. W. H. C. Shaw and J. P. Jefferies. *Ibid.*, 1957, **82**, 8–18.—The mixture formed by irradiation of the provitamins D is separated into groups by chromatography on activated alumina. The material in light petroleum soln. is applied to the column, which is eluted with light petroleum containing 6% of acetone, and the 9-ml fractions fall into three groups,

viz, one containing precalciferol, lumisterol$_2$ and suprasterol$_2$ II, one containing calciferol, tachysterol$_2$ and suprasterol$_2$ I, and one containing normally only the unchanged provitamin ergosterol. The groups are located by applying the $SbCl_3$ test to portions of the eluate. The first two groups are examined spectrophotometrically at 260 and 280 mμ. Only the first two members of each group show absorption at these wavelengths, and from their extinctions the percentage of each component can be determined by two simultaneous equations. The residual provitamins are determined directly, as they are the only compounds related to the vitamins D that are pptd. quant. from dil. ethanol by digitonin. The methods described are unsuitable for use with samples of low potency or in the presence of vitamin A.   A. O. JONES

2809. Determination of vitamin B₁ [thiamine] by the thiochrome method. Y. de Hemptinne and A. Wilmes (Inst. Supérieur des Fermentations de Gand, Ghent, Belgium). *Fermentatio*, 1956, (1), 1–63.—The various chemical, physicochemical, biochemical, and biological methods are outlined, and modifications to a recommended method (*cf.* *Analyst*, 1951, **76**, 127), with special application to cereal products, are proposed. The sample (containing 10 to 40 μg of thiamine) is treated with HCl (0·1 *N*), and the extract is adjusted to a pH of 4·5 to 5 by the addition of Na acetate. Takadiastase (free from thiamine) is added, and the mixture is incubated at 37° overnight, cooled, and filtered. An aliquot of the filtrate is added to a column of Permutit T, and the thiamine is eluted with acid KCl soln. and oxidised to thiochrome by $K_3Fe(CN)_6$. The thiochrome is extracted with *iso*butyl alcohol, the extract is centrifuged and clarified by the addition of ethanol, and submitted to fluorimetric examination.   W. J. WRIGHT

2810. A rapid photometric procedure for the determination of thiamine with 6-aminothymol. K. J. Hayden (Novadel Ltd., St. Ann's Crescent, London). *Analyst*, 1957, **82**, 61–66.—The method described is suitable for the routine analysis of cereal-enrichment materials and pharmaceutical tablets containing 0·5 to 3·5% of thiamine. Tablets are powdered and extracted by the method of the B.P. 1953, the vol. of the final extract being adjusted to contain 20 to 40 μg of thiamine per ml. Enrichment materials are extracted with a known vol. of water, the extract is filtered and, after rejection of the first fifth of the filtrate, an aliquot is diluted with 0·1 *N* HCl to contain 20 to 40 μg per ml. Four calibrated tubes are charged respectively with 1·0, 0·8, 0·7 and 0·6 ml of water and, with the exception of the first, the contents are adjusted to 1 ml with a standard thiamine soln. (1 ml ≡ 100 μg). A fifth tube contains 1 ml of the sample extract. Each tube is treated with alkaline diazotised 6-aminothymol soln. and, after development of the colour and suitable dilution, the extinction is measured in a Spekker absorptiometer with an OB1 filter. The concn. of thiamine in the sample tube is calculated from the two nearest standard readings. The accuracy attained is adequate for routine purposes.   A. O. JONES

2811. Chromatographic method of detecting pyridoxine, pyridoxamine, nicotinic acid and nicotinamide. L. Maiwald and H. Maske. *Hoppe-Seyl. Z.*, 1956, **306** (2–3), 143–144.—*Detection of pyridoxine and pyridoxamine*—The air-dried chromatogram produced from Partridge's mixture (*n*-butanol,

glacial acetic acid and water, 4:1:5) is sprayed first with a diazotising soln. (5 ml of 0·5% sulphanilic acid in 1% HCl and 0·15 ml of 0·5% aq. NaNO₂), and then with Ehrlich's reagent (2% soln. of *p*-dimethylaminobenzaldehyde in 5% HCl) until a uniformly dark yellow colour is produced over the entire paper. After 5 min., the paper is sprayed with conc. aq. NH₃ soln.; this causes disappearance of the yellow coloration and all diazotised compounds are shown by an intense red colour. Pyridoxine (I) and pyridoxamine (II) produce characteristic brown spots; the limit of detection is 5 μg. They may be distinguished from each other by their R_F values. Pyridoxal phosphate is not detectable in quantities < 20 μg, but can be recognised by its R_F value. No other pyridine derivatives are revealed by this method. The air-dried paper is next sprayed first with a 0·2% aq. soln. of Folin's reagent (Na 1:2-naphthaquinone-4-sulphonate) and after 5 min. with conc. aq. NH₃; this changes the coloration due to I and II to emerald green, which is sufficiently vivid to allow the detection of 1 μg of these substances, even though the background may have become coloured blue or grey by the presence of amino acids. *Simultaneous detection of pyridoxine, nicotinic acid and nicotinamide*—The air-dried chromatogram is sprayed with a 1% methanol soln. of 4-chloro-1:3-dinitrobenzene and, after 10 min., with 3 N NaOH; a wine-red colour indicates nicotinamide, while nicotinic acid (III) and I produce orange and pale yellow colours, respectively. The colour due to nicotinamide fades in a few hours, whereas that due to III and I deepens; the limit of detection for these substances is 10 μg. Pyridoxal phosphate, ≮ 30 μg, may give an indefinite yellow colour which fades after a time.   P. HAAS

2812. Chromatographic behaviour of aqueous solutions of ascorbic acid. M. Milletti and A. P. Murroni. *Sperimentale*, 1956, **6** (4–6), 72–96.—The paper chromatography of ascorbic acid and its oxidation products has been studied, in order to establish an exact experimental method. Two methods for showing the reactions of ascorbic acid are described. The aqueous solution is not altered immediately by heating, but after a few days the solution shows the presence of dioxogulonic acid and the methanol complex of ascorbic acid. The difficulty of separating ascorbic acid and dehydroascorbic acid is studied.   C. A. FINCH

2813. Checking the chemical methods for determining ascorbic acid in foodstuffs. E. Bautista Barrera (Inst. Nacíonal de Nutrición, Bogotá). *An. Soc. Biol. Bogotá*, 1956, **7** (4), 152–168.—Four methods for determining ascorbic acid in raw and cooked foodstuffs are compared, with the use of various acid stabilisers for the reduced form of ascorbic acid. It was found that 0·5% of oxalic acid is not an effective stabiliser for all the foodstuffs examined, whereas 2% is effective and gives results similar to those obtained by using 5% HPO₃. The method of Roe *et al.* (*J. Biol. Chem.*, 1943, **147**, 399; 1944, **152**, 511; 1947, **170**, 159), based on the spectrophotometric absorption of the osazones of ascorbic acid, either pure or from mixtures with interfering substances, has been modified. Materials examined include cabbage, spinach, bananas and potatoes.   P. HAAS

See also Abstracts 2644, 2645, 2775, 2776, 2850.

Sanitation

2814. The determination of mercury in air. G. A. Sergeant, B. E. Dixon and R. G. Lidzey (Gov. Lab., Clement's Inn Passage, Strand, London). *Analyst*, 1957, **82**, 27–33.—The method applies to all forms of mercury in air in concn. of ≃ 10 μg per cu. metre, the usually accepted toxic limit. A sampling tube is described and illustrated in which the vapour of Hg and its compounds is absorbed in iodised activated carbon (prep. described), and mercury-bearing dust is trapped in a filter of Stillite filter-wool. In a specially constructed ignition tube the Hg in the mineral wool and the activated carbon is heated and carried by a stream of CO (from heated Na oxalate in the tube) to a circular area of test paper charged with the so-called selenium sulphide (prep. described). The stain produced is compared with standard stains representing known concn. of Hg in air. When the determination of only one contaminant (vapour or dust) is required, only the corresponding absorbent is transferred into the ignition tube. The accuracy of the method is within ± 10%.   A. O. JONES

2815. Analytical methods for the determination of aerosols by the use of membrane ultrafilters. I. Filtration studies on the gravimetric determination. K. Spurný and V. Vondráček (Lab. Hyg. and Epidemiol. Sta., Prague). *Coll. Czech. Chem. Commun.*, 1957, **22** (1), 22–29 (in German).—Diagrams and a description of the apparatus are given. The dependence of the resistance to air flow on the porosity and the mass of trapped aerosol were measured. The efficiency of ultrafiltration was measured by using three filters in series, the first having a porosity of 0·2 to 1·5 μ, the others a porosity of 0·2 μ. With membrane ultrafilters of the series A 024, B 031 and K 044, the two first filters held 100% of a radioactive aerosol; filters of the series K 050 (porosity 0·3 to 0·5 μ) also gave an efficiency of practically 100%. Fractional filtration was carried out through four filters in series, and tested by using a radioactive aerosol. For gravimetric determinations, the filter is weighed before and after the passage of a known vol. of air, after drying for 48 hr. over 96% H₂SO₄. Treatment of the used filter with 2-methoxyethanol renders it transparent, enabling a dispersion count of the aerosol to be obtained. For fractional filtrations, filters of different porosity or of different materials may be used. The method is suitable for aerosol concn. of 0·05 to 500 mg per cu. m. (This paper was published in Czech in *Chem. Listy*, 1956, **50**, 1399.)   C. D. KOPKIN

2816. Determination of strontium-90 activity in water by ion-exchange concentration. C. W. Stanley and P. Kruger (Nuclear Sci. and Engng Corp., Pittsburgh, Pa.). *Nucleonics*, 1956, **14** (11), 114–118.—When the sample, at pH ≃ 7, is passed through a column of Dowex-50 (NH₄⁺ form) the ⁹⁰Sr and ⁹⁰Y are retained. Selective elution is achieved with 5% ammonium citrate soln. At pH 3·8, ⁹⁰Y only is eluted, at pH 6 both ⁹⁰Y and ⁹⁰Sr are eluted. Normal radiochemical purification is applied after the recovery of the nuclides. The recovery from the resin is 100 ± 5%.   G. J. HUNTER

2817. Polarographic determination of lead and zinc in natural waters. T. P. Popova. *Sb. Nauch.-Tekhn. Inform. Min. Geol. i Okhrany Nedr.*, 1955, (1), 129–130; *Ref. Zhur.*, *Khim.*, 1956, Abstr. No.

68,688.—To prevent possible losses of Pb and Zn in storing the sample, and to reduce the vol. of the sample, these elements are co-pptd. in the field with $CaCO_3$. The $CaCO_3$ ppt. carries down Pb completely, and Zn is removed at concn. < 1·5 mg per litre. The $Ca(NO_3)_2$ obtained on solution of the ppt. serves as the polarographic background in the determination of Pb. Zinc is determined polarographically after removal of Pb by co-pptn. with $CaCO_3$ in the presence of ammonium salts. Losses of Zn are caused by the presence of Fe in concn. > 20 or 25 mg per litre. The sensitivity of the method corresponds to 0·01 to 0·02 mg per litre. C. D. KOPKIN

2818. The determination of hypochlorous acid [in water] by titration with methyl orange. E. L. Molt (Lab. Drinkwaterleiding, Rotterdam, Holland). *Chem. Weekbl.*, 1956, **52** (15), 265–267.—In a previous publication (*Ibid.*, 1953, **49**, 164) the methyl orange titration was recommended as the simplest method of determining HOCl, but unsatisfactory results were sometimes obtained. An investigation has shown that the discrepancies are due to different samples of the dye used, and that a strictly linear relation exists between the chlorine content and the amount of methyl orange used only if the dyestuff is of high purity. For titration, the soln. to be tested is acidified with two drops of conc. HCl and the methyl orange soln. (Analar, 1 : 5000) is run in until a pale-pink colour is obtained. As chloramide reacts only slowly, if at all, with methyl orange, this method provides a rapid and reliable means of determining HOCl in soln. containing chloramide. P. HAAS

2819. Recommended methods for the analysis of trade effluents. Methods for the determination of non-volatile matter extractable by light petroleum and the determination of volatile immiscible liquids. Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents. *Analyst*, 1957, **82**, 123–126.—In the determination of non-volatile matter extractable by light petroleum, floating matter, if measurable, is decanted into a separator. The remainder is treated with $MgSO_4$ soln. and then gradually with lime cream until flocculation occurs. The clear liquid is siphoned off, the sediment is dissolved in dil. HCl and the acid liquid is added to the floating matter in the separator together with light petroleum rinsings (50 ml) of the sample bottle. The separator is shaken and the aq. layer is removed for a second extraction. The combined extractions are shaken with anhyd. Na_2SO_4 and filtered, and the residue, after removal of the solvent, is dried on a water bath, weighed and expressed as mg per litre of the sample. The volatile immiscible liquids are determined by the method of Sherratt (*cf. Anal. Abstr.*, 1957, **4**, 1054). A. O. JONES

See also Abstracts 2500, 2856.

Agriculture and Plant Biochemistry

2820. A chromatographic method of analysis for thiols. C. A. Price and C. W. Campbell (Hort. Dept., Purdue Univ., Lafayette, Indiana, U.S.A.). *Biochem. J.*, 1957, **65** (3), 512–516.—The thiol is first treated with N-(4-hydroxy-1-naphthyl)*iso*-maleimide and, after paper-chromatographic development, the product is detected by coupling with tetrazotised *o*-dianisidine, with which it forms an intensely coloured azo product. The technique is

applicable to a variety of thiols and plant material, but is not yet suitable for alkyl thiols. Quantities as small as 0·3 μm-mole are detected, and under optimum conditions 0·1 μm-mole is visible under u.v. light. J. N. ASHLEY

2821. Active principles of derris. III. J. R. Pucci and P. Philipp (Inst. de Pesquisas Tecnol., S. Paulo, Brazil). *An. Ass. Brasil. Quim.*, 1952, [1956], **11**, 181–185.—The determination of rotenone in derris was carried out by three methods, namely, the A.O.A.C. "Official and Tentative Methods of Analysis," 6th Ed. (1945), p. 74; the volumetric method (*cf.* Hornstein, *Brit. Abstr. C*, 1952, 58) and a rapid method (*cf.* Pucci and Philipp, *An. Ass. Quim. Brasil.*, 1951, **10**, 186). Four samples were used and the results were compared. Reasonable concordance was obtained between the various methods. Any major difference was due to the presence of appreciable quantities of resin which were not eliminated during the normal process of analysis. The presence of resin affected the rapid method of analysis and it was necessary to prolong the time of extraction. H. PRITCHARD

2822. Rapid colorimetric estimation of magnesium in soil using a single, self-compensating, reagent. S. N. Edson and R. H. Mills (Dept. of·Soils, Univ. of Florida, Gainesville, U.S.A.). *Chemist Analyst*, 1957, **46** (1), 4–5.—In a modification of Taras' method (*Anal. Chem.*, 1948, **20**, 1157), saturated aq. $Ca(OH)_2$ is used to adjust the pH and compensate simultaneously for the error due to Ca. The self-compensating agent (stable for three months) is prepared by adding 9 vol. of clear lime water to 1 vol. of a 0·01% soln. of Brilliant yellow in methanol - water (1 : 1). The Mg is extracted from the soil with 0·5% Na acetate soln. Beer's law is valid for 2 to 30 p.p.m. of Mg. W. J. BAKER

2823. Flame-photometric determination of exchangeable calcium and magnesium in soils. W. M. Shaw and N. C. Veal (Univ. of Tennessee Agric. Exp. Sta., Knoxville, U.S.A.). *Proc. Soil Sci. Soc. Amer.*, 1956, 328–333.—Soil samples were extracted with N ammonium acetate after which two procedures were employed. In one, acetate, R_2O_3 and $PO_4{}^{3-}$ were eliminated; in the other, the extract was used as such. In each case the Ca^{2+} and Mg^{2+} in soln. were determined flame-photometrically. Greater accuracy was attained with the first method because of mutual interference between Ca^{2+} and Mg^{2+} in ammonium acetate soln. M. F. C. LADD

2824. Determination of alumina in soil. A. G. Kehrig and M. E. Sette (Inst. of Agric. Chem., Min. of Agric., Rio de Janeiro, Brazil). *An. Ass. Brasil. Quim.*, 1953, [1956], **12** (1), 39–57.—Heat the sample (100 ml of a solution in dil. HCl or H_2SO_4, containing ≯ 0·1 g of Al_2O_3) to 80°. Add 5 to 15 ml of 8-hydroxyquinoline reagent (1·4% soln.) and then 2 N ammonium acetate until permanent pptn. begins. Add a further 40 ml of the soln. with agitation, keeping the mixture warm, but without boiling. Allow the ppt. to settle, and add further quantities of 8-hydroxyquinoline reagent until there is a 10-ml excess. Allow the ppt. to settle for 15 min. without heating, then filter through a weighed Gooch crucible, washing the ppt. with boiling water until the yellow colour disappears from the washings, and then with cold water. Dry for 1 hr. at 130° to 135°. This method

glacial acetic acid and water, 4:1:5) is sprayed first with a diazotising soln. (5 ml of 0·5% sulphanilic acid in 1% HCl and 0·15 ml of 0·5% aq. NaNO₂), and then with Ehrlich's reagent (2% soln. of *p*-dimethylaminobenzaldehyde in 5% HCl) until a uniformly dark yellow colour is produced over the entire paper. After 5 min., the paper is sprayed with conc. aq. NH₃ soln.; this causes disappearance of the yellow coloration and all diazotised compounds are shown by an intense red colour. Pyridoxine (**I**) and pyridoxamine (**II**) produce characteristic brown spots; the limit of detection is 5 μg. They may be distinguished from each other by their R_F values. Pyridoxal phosphate is not detectable in quantities < 20 μg, but can be recognised by its R_F value. No other pyridine derivatives are revealed by this method. The air-dried paper is next sprayed first with a 0·2% aq. soln. of Folin's reagent (Na 1:2-naphthaquinone-4-sulphonate) and after 5 min. with conc. aq. NH₃; this changes the coloration due to **I** and **II** to emerald green, which is sufficiently vivid to allow the detection of 1 μg of these substances, even though the background may have become coloured blue or grey by the presence of amino acids. *Simultaneous detection of pyridoxine, nicotinic acid and nicotinamide*—The air-dried chromatogram is sprayed with a 1% methanol soln. of 4-chloro-1:3-dinitrobenzene and, after 10 min., with 3 N NaOH; a wine-red colour indicates nicotinamide, while nicotinic acid (**III**) and **I** produce orange and pale yellow colours, respectively. The colour due to nicotinamide fades in a few hours, whereas that due to **III** and **I** deepens; the limit of detection for these substances is 10 μg. Pyridoxal phosphate, ≪ 30 μg, may give an indefinite yellow colour which fades after a time.   P. HAAS

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applied to acid extracts of soil gave more concordant results than did the standard method of alkaline pptn.   H. PRITCHARD

2825. Methods of soil and plant analysis for molybdenum. E. R. Purvis and N. K. Peterson (Agric. Exp. Station, New Jersey, U.S.A.). *Soil Science*, 1956, **81**, 223–228.—Plant material is digested with HNO_3, then with $HClO_4$ before addition of H_2O_2 and making an aq. HCl soln. Soil is heated with anhyd. Na_2CO_3 at 900° to 950°, the melt is treated with water and HCl, then filtered from silica. *Procedure*—To 100 ml of the test soln. in a 150-ml separating funnel add 1 ml of $FeCl_3$ soln. (4%), 1 ml of $NaNO_3$ soln. (42·5%), 5 ml of NH_4SCN soln. (10%) and 5 ml of $SnCl_2$ soln. (10%), shaking thoroughly after each addition ($FeCl_3$ should be omitted in the analysis of soil samples). Add 10 ml of *iso*propyl ether [previously shaken with 0·1 vol. of $SnCl_2$ soln. - NH_4SCN soln. - H_2O (1:1:1)] and shake by hand 100 times. Separate the phases and determine the transmittance of the ether layer at 475 mμ on a standard colorimeter. Make a blank determination and determine the molybdenum content of the test soln. by reference to a curve prepared from standard soln. containing 20 μg of Mo.   P. HAAS

2826. The use of silver chloride electrodes for the direct determination of chloride ion concentration in soil solutions. N. O. Avakyan. *Doklady Akad. Nauk, ArmSSR*, 1955, **21** (4), 167–169; *Ref. Zhur., Khim.*, 1956, Abstr. No. 68,743.—The silver chloride electrode, in conjunction with the S.C.E., is used as an indicating electrode for the determination of the chloride ion exponent (pCl) and the calculation of the concn. of Cl⁻ in soil soln. The results obtained are compared with data from the potentiometric titration with $AgNO_3$ after tenfold dilution with acetone (*Ref. Zhur., Khim.*, 1955, 26,044). The divergence of the results is ≯ 15%. The superior features of the silver chloride electrode as compared with the glass electrode with a sodium function are that the sensitivity does not depend on the dilution nor on the reaction of the soln., and that in determining pCl the potential of the electrode is very rapidly established.   C. D. KOPKIN

2827. Volumetric method for the determination of phosphorus in mineral fertilisers by the use of oxine. V. M. Litvinchuk and Ya. P. Berkman. *Nauch. Zap. L'vovsk Politekhn. Inst.*, 1955, (29), 81–93; *Ref. Zhur., Khim.*, 1956, Abstr. No. 58,465.— Weigh ≃ 0·3 to 0·4 g of powdered mineral fertiliser, dissolve it in a mixture of HCl and HNO_3 (5:1), evaporate to dryness, treat the dry residue with 10% HCl, cool, transfer to a 250-ml flask, and dilute to volume. For the pptn., to 70 ml of water add 10 ml of HCl (sp. gr. 1·19), 25 ml of the soln. (≡ 5 to 15 mg of P_2O_5), heat to 85°, add 10 ml of $(NH_4)_2MoO_4$ soln. (10%), and slowly, with mixing, add 18 to 20 ml of the standard soln. of 8-hydroxy-quinoline (**I**) (6 g dissolved in 10 ml of conc. HCl, diluted to 1 litre and standardised). Allow the soln. with the ppt. to stand for 5 to 10 min. at 60° to 65°, cool, adjust to vol. with 1·2 N HCl, mix, filter through a dry filter and remove two 50-ml portions of filtrate for the determination of excess of **I** by titration with KBr - $KBrO_3$.
                                     G. BREWER

2828. Use of granulated zinc columns for determining chlorinated organic insecticides. I. Hornstein (Entomology Res. Branch, Agric. Res. Service,

U.S. Dep. of Agric., Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (1), 37–39.—A simple procedure for the partial or complete removal of the organically bound Cl as Cl⁻ by the percolation of an acidified soln. of the insecticide through a granulated zinc column is described. The fraction of Cl⁻ removed is a function of the mol. structure, and when determined by potentiometric titration with $AgNO_3$ it is a reproducible value for a given insecticide.   S.C.I. ABSTR.

2829. Determination of residual *p*-chlorophenyl *p*-chlorobenzenesulphonate [Ovex] in orange pulp. G. J. Butzler, E. N. Luce and R. E. Wing (The Dow Chemical Co., Midland, Mich., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (1), 42–44.—The determination of the acaricide, Ovex, in orange pulp is based on the hydrolysis of Ovex to *p*-chlorophenol and sodium benzenesulphonate. The *p*-chlorophenol, separated by steam-distillation, is converted into the nitroso compound under controlled conditions, interfering materials are separated by chromatography, and the nitrosated *p*-chlorophenol is measured colorimetrically. The method is sensitive to < 5 μg of Ovex, with a recovery of 90%.
                                     S.C.I. ABSTR.

2830. Microchemical and microbiological methods for the determination of OO-dimethyl S-methylcarbamylmethyl phosphorodithioate in olive oil. B. Bazzi, P. de Pietri-Tonelli and R. Santi (Lab. Sperimentale Agrario, Signa, Firenze, Italy). Publ.: Soc. Gen. per l'Ind. Min. e Chim., Milano, 1956, 22 pp.—Microchemical and microbiological methods for the determination of the insecticide OO-dimethyl S-methylcarbamylmethyl phosphorodithioate (Rogor, L 395) in olive oil are described and illustrated with photographs. Both methods require the preliminary extraction of the compound from the olive oil. The min. amount of the insecticide detectable by chemical analysis is about 0·5 p.p.m. with the two following procedures, namely micro-determination of (*i*) phosphorus and (*ii*) methylamine after hydrolysis of the compound. The methylamine is made to react in acid soln. with ninhydrin to give NH_3 and formaldehyde, and the formaldehyde is determined colorimetrically after treatment with chromotropic acid. The min. amount of the insecticide in olive oil detectable by microbiological assay is 0·05 p.p.m. This assay is based on the mortality of adult specimens of *Drosophila melanogaster* Meig. which have come into contact with dried deposits of the insecticide uniformly distributed in Petri dishes.   P. HAAS

2831. Contribution to the polarography of insecticides. Polarographic determination of OO-dialkyl 1-hydroxyethylphosphonates derived from chloral. J. Kováč (Res. Inst. Agrochemical Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1956, **10** (4), 222–226.—OO-Dimethyl 2:2:2-trichloro-1-hydroxyethylphosphate (**I**) (Dipterex) yields a polarographic wave ($E_{\frac{1}{2}} = -$ 1·08 V *vs.* the S.C.E.) in a supporting electrolyte containing 30% by vol. of ethanol, 70% of phosphate buffer solution (pH 6·5) and 0·01% of gelatin. The presence of chloral causes interference. *Procedure*—Dissolve 0·05 g of the sample in ethanol (96%) and make up to 50 ml. Add a 2-ml aliquot and 5 ml of the phosphate buffer solution to the polarographic vessel and register the wave from $-$ 0·4 V.
                                     J. PELIKÁN

See also Abstracts 2627, 2656.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2832. Simple conversion for automatically recording weight changes with an analytical balance. C. Campbell and S. Gordon (Pyrotechnics Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 298–301.—A chainomatic analytical balance can be converted into a continuously recording balance by suspending a steel rod (3·75 in. × 0·25 in.) from one end of the beam into a liquid (*e.g.*, bromobenzene), the displacement of which is proportional to the change in wt. of the sample on the other pan. The rod is attached to the armature of a linear variable differential transformer, which electronically measures and records the deflections of the beam. By varying the liquid density and rod diameter, weighings can be made over the range of 10 to 4500 mg. The accuracy and reproducibility over a range of 400 mg are within 0·25%.   W. J. BAKER

2833. Pipette-controlling and aspirating device with pressure-relieving action. R. C. Backus (Virus Lab., Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1957, **29** (1), 167.—This device is convenient to manipulate and precise in the control of microvolumetric pipettes. It is a small aspirator and consists of a length of rubber tubing held within a rigid barrel. Aspiration is effected by means of a thumb wheel moving in a longitudinal slot. The dimensions are such that pressures inside and out may be equalised instantaneously by momentary release of thumb pressure. The device may be used for filling micro-pipettes, sequential additions of micro quantities, mixing of micro volumes, measurement, by difference, of small quantities, and a number of other operations.   L. S. ADLER

2834. Control device for precisely regulating flow of air or gas at low rates. W. H. McKinney (Koppers Co., Oil City, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 318.—This device for continuous control comprises an orifice-nipple inside which is fixed a 12-in. spiral of metal capillary-tubing ($\simeq$ 0·01 in. internal diam.), the lower end of which leads to the apparatus, *e.g.*, for oil-oxidation tests. A two-stage reduction of pressure followed by a low-pressure valve ensures that the nipple will deliver, *e.g.*, **13** litres per hr. at 30 lb. per sq. in. or 3 litres at 7 lb. pressure. For lower rates of flow a longer capillary tube is required.   W. J. BAKER

2835. A continuous ether extractor. K. J. Jensen and R. W. Bane (Argonne National Lab., Lemont, Illinois). *Analyst*, 1957, **82**, 67–70.—The ether extractor described and illustrated effects continuous extraction of U from its nitrate and minimises manipulations involving hazards from radioactivity. A device enables the soln. from which the U has been extracted to be disposed of directly and safely into a shielded active-waste container without dismantling the apparatus. Also an aliquot of this soln. can be segregated for spectrographic or other confirmation that all the U has been extracted, or for further analysis. The sample of U in the form of a dried nitrate salt dissolved in the minimum amount of HNO_3 saturated with NH_4NO_3 is extracted with ether and then determined gravimetrically by pptn. with aq. NH_3 and ignition to

U_3O_8 at 850°. Under the specified conditions the extraction is practically complete when the U extracted is 200 mg or more.   A. O. JONES

2836. A new suction filter-funnel. H. A. Kamphausen (The Univ., Melbourne, Australia). *Chem. & Ind.*, 1957, (9), 249–250.—The 60° filter-funnel has a double glass wall, into the outer surface of which a side-arm is sealed. The stem of the glass-nail projects $\simeq$ 1 cm above the inner stem of the funnel. The nail-head is shallowly corrugated (to make the filter-paper secure) and its rim is accurately circular. This funnel dispenses with the need for special filter-tubes.   W. J. BAKER

2837. Determination of impurities in filter-paper. H. Weisz (Univ. of Birmingham, England). *Analyst*, 1957, **82**, 132–133.—The ring-oven technique (*cf. Anal. Abstr.*, 1954, **1**, 2604; 1955, **2**, 834) serves to determine the impurity in filter-paper. Selective extraction is effected by choice of solvent, and classification of types of impurity is thus possible. For example, with 0·02 *M* HCl (highly purified) as solvent, heavy metals are concentrated in the ring zone. The dried paper is cut and one-half is sprayed with $K_4Fe(CN)_6$ soln. to detect Fe and the other half is bathed in ammonium sulphide soln. to fix the heavy metals. The excess of reagent is washed away and the paper is treated with $AgNO_3$ soln. to replace invisible sulphides (*e.g.*, ZnS, MnS) by Ag_2S. Particular ions can be detected by spraying with the appropriate reagent. Chloride, the other most common impurity, is detected by washing it into the ring zone with water, bathing the dried paper in $AgNO_3$ soln., removing the excess of reagent and developing the ring with ammonium sulphide. The method is useful for following the purification of paper for chromatography and electrophoresis.   A. O. JONES

2838. Device for regulating small flow rates in chromatographic columns. L. H. Gevantman, R. K. Main and L. M. Bryant (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 170.—The device consists of an auxiliary column containing powdered glass, which is fitted below the chromatographic column by means of a ground glass joint. Flow rates of 3 to 4 ml per hr. with fluctuations not exceeding 3% for periods of up to 16 hr. were readily obtained by changes in the dimensions of the auxiliary column and of the powdered glass grains.   L. S. ADLER

2839. Fraction cutter for large-scale column chromatography. J. E. Philip and J. R. Schenck (Abbott Lab., North Chicago, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 170.—An all-glass unit is described which is especially useful for collecting fractions of 0·5 to 20 litres. It consists of a straight vertical tube and a T-tube, in whose vertical limb is contained a hollow glass float, which acts as a shut-off valve. Both tubes are set in the receiver. The chromatographic eluate flows along the horizontal limb of the T-tube, down past the float into the receiver. When the level of eluate in the receiver reaches the bottom end of the higher of the two tubes, the vertical limb of the T fills up and the float valve acts. The unit can then be taken out of circuit.   L. S. ADLER

2840. The chromatimer or chromatograph monitor. G. G. Blake (Sydney Univ., N.S.W., Australia). *Chem. & Ind.*, 1957, (9), 248–249.—A simple device

for automatically stopping the development of one or more chromatograms is described and illustrated.   W. J. BAKER

2841. The micro-flame detector in gas - liquid partition chromatography: correlation of response with heats of combustion. J. I. Henderson and J. H. Knox (Univ., Edinburgh). *J. Chem. Soc.,* 1956, 2299–2302.—Gas - liquid partition chromatography is carried out with N or CO_2 as carrier gas. Hydrogen is added to the gas stream as it emerges from the column and the resulting mixture is burnt in a draught-free housing in contact with a thermocouple. The temp. rise of the thermocouple during the combustion of any band is proportional to the rate of liberation of heat in the combustion of the band. The method is more suitable than the thermal conductivity detector for the analysis of mixtures containing substances of higher mol. wt. and higher heats of combustion, such as are found in petroleum distillates.   N. E.

2842. The quantitative measurement and transfer of samples in gas chromatography. S. W. S. McCreadie and A. F. Williams (Res. Dept., Nobel Div., I.C.I. Ltd., Stevenston, Ayrshire, Scotland). *J. Appl. Chem.,* 1957, **7** (1), 47–48.—A simple device is described to enable a sample to be transferred easily and quantitatively to the column used in gas chromatography.   K. A. PROCTOR

2843. Sample introduction system for gas chromatography. H. M. Tenney and R. J. Harris (Esso Standard Oil Co., Baton Rouge, La., U.S.A.). *Anal. Chem.,* 1957, **29** (2), 317–318.—A capillary pipette (micro or macro) containing the sample is inserted into the connecting tube to the column until the slightly larger handle forms a seal with a neoprene ring. The pipette is then brought under the pressure of the system and passed through the valve until its tip projects through the orifice seat. The immediate pressure-drop across the capillary sweeps the sample into the column, and the pipette can be removed without disturbing the gas flow. The device operates with high precision for liquids and gases.   W. J. BAKER

2844. Ionisation gauge detector for gas chromatography. S. A. Ryce and W. A. Bryce (Chem. Dept., Univ. of British Columbia, Vancouver, Canada). *Nature,* 1957, **179,** 541.—A very small fraction ($< 0.5\%$) of the helium gas stream from a chromatographic column passes into an R.C.A. 1949 ionisation gauge with the glass envelope modified to allow the gas to flow between the gauge components. The p.d. between the filament and grid is adjusted to $\simeq$ 18 V, well below the ionisation potential of He (24·5 V). Ionisation current results from the passage of substances of lower ionisation potential and is amplified and recorded. The sensitivity obtained is at least 200 times that of a thermistor-type conductivity cell, and the gauge is insensitive to ambient temp. changes and also to changes in pressures and flow rate in the main gas stream. Further sensitivity might be obtained by using screen and suppressor grids and by replacing the tungsten filament by one of iridium.   K. A. PROCTOR

2845. Development of a continuous gas chromatographic analyser for sludge-digestion studies. W. N. Grune, J. Y. Carter, jun., and J. P. Keenan (Sanitary Engng Res. Lab., Georgia Inst. of Technol., Atlanta, Ga., U.S.A.). *Sewage Ind. Wastes,* 1956, **28** (12),

1433–1442.—An apparatus has been developed by means of which an automatically controlled gas-sampling valve continuously samples the gas stream and passes discrete samples for elution analysis into a continuous carrier gas stream (N or He), which moves the components for separation through a chromatographic column (several types have been investigated). The basic analyser comprises a thermal conductivity cell, in which the carrier gas passes through the reference side. Differences in thermal conductivity are recorded by the upset of balance of a Wheatstone bridge circuit. (14 references.)   S.C.I. ABSTR.

Optical

2846. Sample handling for qualitative infra-red microspectroscopy. E. D. Black, J. D. Margerum and G. M. Wyman (Quartermaster Research & Development Center, Natick, Mass., U.S.A.). *Anal. Chem.,* 1957, **29** (1), 169.—Two simple methods, requiring no specialised equipment, are described. In the first, for non-volatile liquids, the sample is carried as a thin film, adhering by surface tension to a rigid disc of thin plastic or glass, across a hole drilled in the centre of the disc. In the second method, for volatile liquids, the sample cell consisted of a loop of thin platinum wire sandwiched between potassium bromide discs. Good spectra were obtained for known substances by both methods. The methods are qualitative only, since the thickness of the film of sample is known only approximately.   L. S. ADLER

2847. Quantitative infra-red analysis of solids in potassium bromide using an internal standard. S. E. Wiberley, J. W. Sprague and J. E. Campbell (Rensselaer Poly. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.,* 1957, **29** (2), 210–213.—If KSCN [0·1 to 0·2% (w/w)] is used as an internal standard in the KBr disc (4 g), the necessity for measuring sample thickness, as in previous methods (*cf. Anal. Abstr.,* 1956, **3**, 611), is eliminated and the construction of calibration curves is simplified. Provided that the KSCN, KBr and the sample are finely ground in a vibrator-grinder before being pressed into pellets, reproducible quant. results can be obtained for the i.r. absorbance ratios of the selected band of the sample and the 4·7-μ band of the internal standard. Results for the determination of the acetate content of poly(vinyl acetate) - poly(vinyl chloride) copolymer and the free fatty acid in aluminium soap are reported. In both instances measurements are made on the CO band at 5·8 μ.   W. J. BAKER

2848. Raman spectrometry. I. Construction of a photo-electric recording Raman spectrometer. G. Michel and G. Duyckaerts (Univ. Liège, Belgium). *Spectrochim. Acta,* 1957, **8** (6), 356–373.—The spectrometer incorporates a Toronto-type helical mercury arc source, an adapted Huet B III spectrograph as monochromator and an amplifier of the authors' design feeding into a Brown recorder. The principles of optical and electronic design for optimum performance are discussed and the circuit diagram is given. A signal-to-noise ratio varying from 500:1 at 992 cm^{-1} to 350:1 at 459 cm^{-1} was obtained with a time constant of 4 sec. The spectra include a resolution test showing good separation of the 992-cm^{-1} band of benzene from the 1001-cm^{-1} band of toluene. Intensity measurements show a mean relative error $\not> 2\%$.   E. G. CUMMINS

2849. Rayleigh interferometer for the analysis of liquids. E. Grunwald and B. J. Berkowitz (Florida State Univ., Tallahassee, Fla., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 124–129.—The Rayleigh interferometer is ideally suited, because of its sensitivity to refractive index differences $< 1 \times 10^{-6}$, for the precise measurement of the composition of two-component liquid mixtures, and of solute concn. in dil. solutions. Its use for this purpose, however, has been hindered by, on the one hand, the difficulty of locating the zero-order interference fringe without elaborate prior calibration and, on the other, the difficulty of handling volatile liquids. Workable solutions to both problems are reported here. A method for the unambiguous identification of the zero-order fringe is described and expounded mathematically. It involves the use of a tungsten light source, and, in addition, any two convenient auxiliary monochromatic light sources of known wavelength. For volatile liquids a special interferometer cell was devised and used for the analysis of dioxan - water mixtures, when an accuracy within 0·006% by wt. was achieved.

L. S. ADLER

Thermal

2850. Improved constant-temperature bath for the active oxygen method fat stability apparatus. W. F. Schroeder and J. W. Draper (The HumKo Co., Memphis, Tennessee, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1956, **33** (12), 628–630.—The bath consists of an insulated electrically heated brass block provided with cavities for the accommodation of a thermoregulator, thermometers, and 24 sample tubes. This bath has given satisfactory service over a prolonged period. Under working conditions, a constant uniform temp. ($\pm$ 0·1°) can be maintained in the oil contained in all the tubes. Technical details are discussed. Later models have been constructed in aluminium.

P. S. ARUP

2851. Performance of a pen-recording Chevenard thermobalance. E. L. Simons, A. E. Newkirk and I. Aliferis (General Electric Res. Lab., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 48–54.—The sensitivity and reliability of a commercially available instrument were examined over a period of 18 months. It was found that the determination of weight changes is subject to both random and bias errors. The random error is not large and may be represented by a standard deviation. Bias errors, arising from (*i*) dependence of the calibration factor on the range of the chart paper over which it is measured, and (*ii*) the apparent gain in wt. of a sample, with increase in temp., may be appreciable. Their magnitude may be reduced relatively easily, but their complete elimination is difficult. Certain recommendations for the efficient operation of these instruments are made.

L. S. ADLER

2852. Analytical applications of a differential thermal analysis apparatus. P. D. Garn and S. S. Flaschen (Bell Telephone Lab., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 271–275.—An improved apparatus is described and illustrated, and its use in determining decomposition or transition temp. of samples of ceramic materials is discussed. The use of platinum cups increases the recording sensitivity provided that the cup thickness ensures thermal equilibrium. Thermograms are shown for samples, from different sources, of $MgCO_3$, talc, K maleate and for mixtures of quartz and K_2SO_4; the curves for K maleate differ according to whether the salt is prepared from maleic anhydride or diethyl maleate. The phase-equilibrium diagram for the ferro-electric system $KNbO_3$ - $KTaO_3$ is constructed from differential thermal analysis data.

W. J. BAKER

2853. Thermochemical titrations. Enthalpy titrations. J. Jordan and T. G. Alleman (Pennsylvania State Univ., University Park, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 9–13.—Enthalpy titrations are defined as volumetric methods depending on heats of reaction. Automatic titrations are presented which, in an adiabatic system, yield a graph of temp. change against concn. of added reagent. These titrations were applied to the accurate evaluation of heats of chelation of bivalent cations with EDTA (tetrasodium salt); the results were in good agreement with the best available data. By reversing the procedure, the method was applied to the quant. determination of bivalent cations in soln., both singly and in admixture, *e.g.*, Ca and Mg. The accuracy of the method, which is applicable to concn. as low as $5 \times 10^{-4} M$, is within about $\pm 3\%$.

L. S. ADLER

Electrical

2854. Versatile paper-electrophoresis apparatus. H. Jonas (Virginia Univ. Med. Sch., Charlottesville, U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (1), 135-141.—The apparatus described can be used for continuous two-dimensional separation and for strip experiments. Provisions are made for maintaining constant voltage, temp., pH of electrolyte, sample and buffer flow.

W. H. C. SHAW

2855. Some investigations of the sensitivity and resolving power of a simple d.c. amplifier polarograph. D. R. Curry and J. T. King-Cox [Bragg Lab. (N.O.I.D.), Janson St., Sheffield, England]. *Analyst*, 1957, **82**, 128–132.—Comparative tests have been reported (*cf.* Ferrett *et al.*, *Analyst*, 1956, **81**, 506) on the Univector unit of the Cambridge Instrument Co. Ltd., the Mervyn - Harwell square-wave polarograph, and the single-sweep cathode-ray polarograph of Southern Instruments Ltd. These results are now compared with the performance of the Tinsley recording polarograph, mark 15/6, with a slightly modified circuit. Details of the tests for sensitivity and resolution are given. The comparison showed that in view of the complexity and cost of the new precision instruments the performance of the Tinsley instrument is of a high order.

A. O. JONES

2856. Use of wide-bore dropping-mercury electrode and zinc reference electrode for continuous polarography. R. Briggs, F. S. Davies, G. V. Dyke and G. Knowles (Water Pollution Res. Lab., Stevenage, Herts., England). *Chem. & Ind.*, 1957, (8), 223–224.—To extend the period of reproducibility of the results in polarographic analysis, the dropping-mercury electrode has a bore of 0·8 mm instead of the usual 0·04 mm and is inclined upwards at 45°. Mercury is supplied at a constant rate of 6 ml per hr. and at one drop per 2·5 sec. by keeping the mercury surface in the reservoir 15 cm above the

electrode tip and maintaining the level by a float switch. The mercury flows down 30 cm of plastics tubing (3 mm in diam.), through 25 cm of glass tubing (0·2 mm bore), and by a plastics connection to the wide-bore capillary electrode. The second electrode is a zinc rod in a buffer soln. (pH 5·5), which communicates with the water through a sintered-glass disc. It has a potential of − 1·0 V v.s. the S.C.E. The currents of the wide-bore dropping-mercury electrode are 15 times as great as those from the usual type. The electrode has been used for measuring the concn. of dissolved O in sewage effluent containing colloidal and suspended material.   W. J. WRIGHT

2857. Use of a wax-impregnated graphite electrode in polarography. V. F. Gaylor, A. L. Conrad and J. H. Landerl (Standard Oil Co., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 224–228.—A wax-impregnated graphite rod yields more accurate polarographic measurements in both oxidising and reducing media than does a plain graphite electrode. Residual currents are minimised, reproducibility is improved and the sensitivity of measurement in small concn. ($\equiv 10^{-5}\,M$) is increased tenfold or more in a stirred soln. The values of $E_{\frac{1}{2}}$ for the oxidation waves of phenols, mono- and di-amines and quinonoid compounds, and for the reduction waves of Ag^+ and Pb^{2+} can be determined to within 0·01 V. Diffusion currents are proportional to concn. and can be utilised for quant. analysis, the coeff. of variation being $\simeq 2\%$ in unstirred soln. With proper selection of impregnating agents (ceresin, opal and castor waxes) and rod diameter, the electrode can be used in aq. or non-aq. soln. and, in stirred soln., it is specially applicable to the determination of very small concn. of O.   W. J. BAKER

2858. Behaviour of rotating gold micro-electrodes. F. Baumann and I. Shain (Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1957, **29** (2), 303–306.—Current - voltage curves obtained with rotating gold micro-electrodes are affected by electrode-surface condition (oxide films) and impurities in the electrolyte. Because of this gold oxide film, the useful range of potential of gold electrodes is − 0·2 to + 0·8 V in O-free 1 M $HClO_4$. If the electrodes are pretreated consistently and complexing anions are absent, gold is more resistant to oxidation than is platinum, so that direct polarographic determinations of Cr^{6+} (concn. 10^{-4} to $10^{-6}\,M$) in 1 M $HClO_4$ can be made at + 0·4 V without interference from the reduction of O. The preferred pretreatment is 15-sec.

anodisation at + 2·5 V, followed by 5-sec. treatment at 0 V. (*Cf. Anal. Abstr.*, 1954, **1**, 2028, 2030.)   W. J. BAKER

2859. Cleaning of capillaries for use in polarography. F. L. Lambert (Occidental Coll., Los Angeles, Calif., U.S.A.). *Chemist Analyst*, 1957, **46** (1), 10.—Fouling of the capillary tip and bore during polarography, especially of organic compounds at negative voltages in aq. ethanolic soln., can be avoided by a cleaning process that involves suction with ethanol, H_2O, warm HNO_3 (1:1), H_2O, warm dil. aq. KOH and hot H_2O in that order. The tip can be cleaned superficially, without detaching the capillary from the polarogram, by immersion in warm HNO_3 (1:1) while the mercury is dropping, followed by a rinse with H_2O and organic solvents.   W. J. BAKER

2860. Electrometric method for the determination of rH and pH *in vitro*, and in biological fluids *in vivo*. M. Dante (Anal. Chem. Inst., Florence Univ., Italy). *Sperimentale*, 1956, **6** (4–6), 97–105.—A thermionic valve potentiometer is used with a chain of three electrodes—a mixed calomel - platinum electrode and a glass electrode. By using the calomel electrode for comparing alternately the two others, it is possible to measure rH and pH extremely rapidly, with only a little liquid. To reduce errors, a thermostat accurate to ± 0·5°, a gas-holder reducing variations in the pressure of gas dissolved in the liquid and eliminating the presence of oxygen, and a cell with an internal silicone coating and poly(vinyl chloride) tubes are used.   C. A. FINCH

2861. Electron diffraction; its application to chemical analysis. B. S. Cooper and H. E. Bullen (G.E.C. Research Laboratories, Wembley, Middx.). *G.E.C. Journal*, 1956, **23** (3), 130–136.—An electron diffraction camera, suitable for use with the various types of sample likely to occur in an industrial research laboratory, is described. Notes are given on the preparation and handling of specimens, and on the various types of electron diffraction pattern likely to be obtained and their interpretation. Examples of problems in which the instrument has been successfully employed are—(*i*) the detection of a film of graphite on a thermionic cathode coating, the film being too thin to detect by X-ray diffraction, (*ii*) the identification of a deleterious film on the surface of certain batches of commercial nickel sheet as $2CaSO_4.H_2O$, and (*iii*) the identification of the surface contaminant on a sample of gold which proved difficult to amalgamate.   B. S. COOPER

ERRATUM.—July (1957) issue, abstract 2122, line 8. *For* "1954" *read* "1955."

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	.	.	a.c.	milli-equivalent	.	milli-equiv.
ampere	.	.	amp.	milligram	.	mg
Ångström unit	.	.	Å	millilitre	.	ml
anhydrous	.	.	anhyd.	millimetre	.	mm
approximate, -ly	.	.	approx.	millimicrogram	.	$m\mu g$
aqueous	.	.	aq.	millimolar	.	mM
atmospher-e, -ic.	.	.	atm.	millivolt	.	mV
boiling-point	.	.	b.p.	minute (time)	.	min.
British thermal unit	.	.	B.Th.U.	molar (concentration)	.	M
calorie (large)	.	.	kg-cal.	molecul-e, -ar	.	mol.
calorie (small)	.	.	g-cal.	normal (concentration)	.	N
centimetre	.	.	cm	optical rotation	.	α
coefficient	.	.	coeff.	ounce	.	oz
concentrated	.	.	conc.	parts per million	.	p.p.m.
concentration	.	.	concn.	per cent.	.	%
constant	.	.	const.	per cent. (vol. in vol.)	.	% (v/v)
corrected	.	.	(corr.)	per cent. (wt. in vol.)	.	% (w/v)
crystalline	.	.	} cryst.	per cent. (wt. in wt.)	.	% (w/w)
crystallised	.	.		potential difference	.	p.d.
cubic	.	.	cu.	precipitate (as a noun)	.	ppt.
current density	.	.	c.d.	precipitated	.	pptd.
cycles per second	.	.	c/s	precipitating	.	pptg.
density	.	.	ρ	precipitation	.	pptn.
density, relative	.	.	d or wt. per ml	preparation	.	prep.
dilute	.	.	dil.	qualitative, -ly	.	qual.
direct current	.	.	d.c.	quantitative, -ly	.	quant.
distilled	.	.	dist.	recrystallised	.	recryst.
ethylenediaminetetra-acetic				refractive index	.	n_λ^t
acid	.	.	EDTA	relative band speed	.	R_F
electromotive force	.	.	e.m.f.	relative humidity	.	r.h.
equivalent	.	.	equiv.	revolutions per minute	.	r.p.m.
gram	.	.	g	saponification value	.	sap. val.
gram-molecule	.	.	mole	saturated calomel electrode	.	S.C.E.
half-wave potential	.	.	$E_{\frac{1}{2}}$	second (time)	.	sec.
hour	.	.	hr.	soluble	.	sol.
hydrogen ion exponent	.	.	pH	solution	.	soln.
infra-red	.	.	i.r.	specific gravity	.	sp. gr.
insoluble	.	.	insol.	specific rotation	.	$[\alpha]_\lambda^t$
international unit	.	.	i.u.	square centimetre	.	sq. cm
kilogram	.	.	kg	standard temp. and pressure	.	s.t.p.
kilovolt	.	.	kV	temperature	.	temp.
kilowatt	.	.	kW	ultra-violet	.	u.v.
liquid	.	.	liq.	vapour density	.	v.d.
maxim-um, -a	.	.	max.	vapour pressure	.	v.p.
melting-point	.	.	m.p.	volt	.	V
microgram	.	.	μg (not γ)	volume	.	vol.
microlitre	.	.	μl	watt	.	W
micromole	.	.	μmole	wavelength	.	λ
micron	.	.	μ	weight	.	wt.
milliampere	.	.	mA			

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	.	$>$	less than	$<$
not greater than	.	$\not>$	not less than	$\not<$
is proportional to	.	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II}, Mo^V. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

ANALYTICAL ABSTRACTS

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